# MILLING METHODS

1939

A. I. M. E.

A5
vol. 134
N/C

# TRANSACTIONS

OF THE

# AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS

(INCORPORATED)

and Petroleum

## Volume 134

---

# MILLING METHODS
## 1939

Sponsored by the
ROCKY MOUNTAIN FUND

---

PAPERS AND DISCUSSIONS PRESENTED AT MEETINGS HELD AT NEW YORK, FEB.
18–21, 1935; FEB. 17–21,1936; FEB. 15–19; 1937; FEB. 14–17, 1938;
FEB. 13–16, 1939; AND AT TUCSON, NOV. 1–5, 1938.

---

PUBLISHED BY THE INSTITUTE
AT THE OFFICE OF THE SECRETARY
29 WEST 39TH STREET
NEW YORK, N. Y.

Copyright, 1939, by the
American Institute of Mining and Metallurgical Engineers
(Incorporated)

---

PRINTED IN THE UNITED STATES OF AMERICA

THE MAPLE PRESS COMPANY, YORK, PA.

# FOREWORD

This volume, like Volume 112 of the TRANSACTIONS, on Milling Methods, is sponsored by the Rocky Mountain Fund, through an appropriation made on recommendation of the Committee, of which the members are Henry Krumb, chairman, Harvey S. Mudd and George Otis Smith. Continued progress in the art and advance in the study of the theoretical principles of mineral dressing make it advisable to extend the record so as to bring it up to date.

The purpose of the present volume is to bring together into a single work as many as possible of the milling papers presented to the Institute since the publication of the previous volume on Milling Methods in 1934. Through the continuous efforts of the personnel of many laboratories and of countless individual investigators there is an ever expanding body of knowledge being made available for new as well as old applications in this field of technical endeavor, of which the world at large is the beneficiary. It is believed that the material selected is representative of the present trend of investigations in the field of ore dressing, and it is hoped that its scope is sufficiently broad to render it of interest to all readers.

It has been the difficult task of the Committee on Papers and Publications to select the contents of this volume from a large number of excellent papers, some of which could not be included because of limitation of space.

Those who have served as chairmen of the Committee on Milling Methods since 1934 are: Charles E. Locke from 1935 to 1937, Will H. Coghill, 1938 and E. W. Engelmann, 1939 and 1940. It is impossible to mention the names, individually, of those who have cooperated and assisted in preparing the material. However, the vice chairmen and committee join with me in extending thanks to all who have hepled to make this volume possible.

E. W. ENGELMANN, *Chairman*,
Committee on Milling Methods.

MAGNA, UTAH
*July* 19, 1939

# A.I.M.E. OFFICERS AND DIRECTORS

**For the year ending February, 1940**

PRESIDENT AND DIRECTOR
Donald B. Gillies, Cleveland, Ohio

PAST PRESIDENTS AND DIRECTORS
R. C. Allen, Cleveland, Ohio
D. C. Jackling, San Francisco, Calif.

TREASURER AND DIRECTOR
Karl Eilers, New York, N. Y.

VICE-PRESIDENTS AND DIRECTORS
H. G. Moulton, New York, N. Y.
Harvey S. Mudd, Los Angeles, Calif.
Paul D. Merica, New York, N. Y.
Wilfred Sykes, Chicago, Ill.
William B. Heroy, Houston, Texas
Henry Krumb, New York, N. Y.

DIRECTORS
John M. Boutwell, Salt Lake City, Utah
Charles Camsell, Ottawa, Ont., Canada
Erle V. Daveler, New York, N. Y.
Chester A. Fulton, Baltimore, Md.
H. T. Hamilton, New York, N. Y.
A. B. Jessup, Waverly, Pa.
W. E. McCourt, St. Louis, Mo.
James T. Mac Kenzie, Birmingham, Ala.
W. M. Peirce, Palmerton, Pa.
Brent N. Rickard, El Paso, Texas
Le Roy Salsich, Duluth, Minn.
Francis A. Thomson, Butte, Mont.
H. Y. Walker, New York, N. Y.
George B. Waterhouse, Cambridge, Mass.
Henry D. Wilde, Houston, Texas
William Wraith, New York, N. Y.
L. E. Young, Pittsburgh, Pa.

SECRETARY
A. B. Parsons, New York, N. Y.

---

DIVISION CHAIRMEN—Acting as Advisers to the Board
R. H. Leach (Institute of Metals), Bridgeport, Conn.
W. H. Geis (Petroleum), Los Angeles, Calif.
John Hunter Nead (Iron and Steel), East Chicago, Ind.
C. A. Gibbons (Coal), Nanticoke, Pa.
Francis A. Thomson (Education), Butte, Mont.
M. M. Leighton (Industrial Minerals), Urbana, Ill.

STAFF IN NEW YORK

*Assistant Secretaries*
Edward H. Robie
Louis Jordan
Chester Naramore

*Assistant Treasurer*
H. A. Maloney

*Assistant to the Secretary*
E. J. Kennedy, Jr.

*Manager, "Mining and Metallurgy"*
John T. Breunich

# CONTENTS

PAGE
Foreword. By E. W. ENGELMANN . . . . . . . . . . . . . . . . . . . . . . . 3
A.I.M.E. Officers and Directors. . . . . . . . . . . . . . . . . . . . . . . 4

## PAPERS

Principles of Flotation, IV—An Experimental Study of Influence of Sodium Sulfide, Alkalies and Copper Sulfate on Effect of Xanthates at Mineral Surfaces. By IAN WILLIAM WARK AND ALWYN BIRCHMORE COX. (T.P. 659, with discussion). . . . . . . . . . . . . . . . . . . . . . 7
Principles of Flotation, V—Conception of Adsorption Applied to Flotation Reagents. By IAN WILLIAM WARK and ALWYN BIRCHMORE COX. (T.P. 732, with discussion). . . . . . . . . . . . . . . . . . . . . . 26
Principles of Flotation, VI—Influence of Temperature on Effect of Copper Sulphate, Alkalies and Sodium Cyanide on Adsorption of Xanthates at Mineral Surfaces. By IAN WILLIAM WARK and ALWYN BIRCHMORE COX. (T.P. 876, with discussion). . . . . . . . . . . . . . . . . . . . . . 41
Principles of Flotation, VII—Mercaptobenzthiazole as a Flotation Agent. By IAN WILLIAM WARK and KEITH LEONARD SUTHERLAND. (T.P. 1007) . . . 53
Conditioning Surfaces for Froth Flotation. By JAMES E. NORMAN and OLIVER C. RALSTON. (T.P. 1074) . . . . . . . . . . . . . . . . . . . . . . 65
New Flotation Reagents. By R. S. DEAN and A. B. HERSBERGER. (T.P. 605) 81
Froth Flotation of Fluorspar. By DAVID R. MITCHELL, HENRY EMMETT GROSS and H. E. OEHLER. (T.P. 999). . . . . . . . . . . . . . . . . . . . . . 89
Study of the Flotative Properties of Hematite. By W. E. KECK, G. C. EGGLESTON and W. W. LOWRY. (T.P. 763, with discussion) . . . . . . . . . . 102
Study of the Flotative Properties of Magnetite. By W. E. KECK and PAUL JASBERG. (T.P. 801, with discussion) . . . . . . . . . . . . . . . . . . 129
Flocculation and Clarification of Slimes with Organic Flocculants. By GEORGE R. GARDNER and KENNETH B. RAY. (T.P. 1052, with discussion) . . . . 146
Mineralogical Characteristics Affecting the Concentration of a Semioxidized Lead-silver Ore. By R. E. HEAD. (T.P. 939, with discussion). . . . . . 169
Oil-air Separation of Nonsulphide and Nonmetal Minerals. By ARTHUR F. TAGGART, G. R. M. DEL GIUDICE, A. M. SADLER and M. HASSIALIS. (T.P. 838, with discussion). . . . . . . . . . . . . . . . . . . . . . 180
Cyanide Process Based on the Simultaneous Dissolution and Adsorption of Gold. By T. G. CHAPMAN. (T.P. 1070, with discussion). . . . . . . . . . . . 207
Milling Developments at the Benguet Consolidated Plant. By J. M. MORRIS. (T.P. 675, with discussion). . . . . . . . . . . . . . . . . . . . . . 224
Milling Practice at Demonstration Gold Mines Ltd., Philippine Islands. By GEORGE A. BELL. (T.P. 1017). . . . . . . . . . . . . . . . . . . . . . 236
The Achotla Chloridizing Mill. By H. P. ALLEN. (T.P. 773, with discussion) . 243
Physical Characteristics of Gold Lost in Tailings. By R. E. HEAD. (T.P. 674, with discussion). . . . . . . . . . . . . . . . . . . . . . 256
Electrocapillary Amalgamation. By ORSON CUTLER SHEPARD. (T.P. 676, with discussion). . . . . . . . . . . . . . . . . . . . . . 265
Modern Trends in Classification. By C. K. MCARTHUR. (T.P. 815) . . . . . 274

PAGE

Use of the Coercimeter in Grinding Tests. By Fred D. DeVaney and Will H. Coghill. (T.P. 862, with discussion) . . . . . . . . . . . . . . . . . . 282
Grindability and Grinding Characteristics of Ores. By Fred C. Bond and Walter L. Maxson. (T.P. 888, with discussion) . . . . . . . . . . . . 296
Magnetite as a Standard Material for Measuring Grinding Efficiency. By R. S. Dean. (T.P. 660) . . . . . . . . . . . . . . . . . . . . . . . . 324
Rod-mill Practice at Ray Mines Divisions, Kennecott Copper Corporation. By F. J. Tuck. (T.P. 994) . . . . . . . . . . . . . . . . . . . . . . 327
Improvements in Fine Grinding and Classification at the Hollinger Consolidated Gold Mines Ltd. By H. W. Hitzrot. (T.P. 1088) . . . . . . . . . . . 331
Closed-circuit Grinding of Cement Raw Materials at Leeds. By T. B. Counselman. (T.P. 1096, with discussion) . . . . . . . . . . . . . . . . . . . 344
65-mesh Grinding in Closed Circuit with Stainless-steel Screens. By Walter M. Stephen. (T.P. 901, with discussion) . . . . . . . . . . . . . . . 361
The "Electric Ear," a Device for Automatically Controlling the Operation of Grinding Mills by Their Sound. By Harlowe Hardinge. (T.P. 1076, with discussion) . . . . . . . . . . . . . . . . . . . . . . . . . . 371
First Magnetic Roasting Plant in the Lake Superior Region. By E. W. Davis. (T.P. 731, with discussion) . . . . . . . . . . . . . . . . . . . . . . 389
Selective Electrostatic Separation. By Herbert Banks Johnson. (T.P. 877, with discussion) . . . . . . . . . . . . . . . . . . . . . . . . . . 409
Comparative Washing Efficiencies in Cyaniding—The Washing Tray Thickener versus the Conventional Countercurrent Decantation Plant. By Neil O. Johnson. (T.P. 1082) . . . . . . . . . . . . . . . . . . . . . . . . . 424
Milling Methods at New Cornelia. By L. M. Barker. (T.P. 1015) . . . . . 434
Index . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 453

**Milling Papers in Volume 129**

Log Washers in the Aggregate and Flux-stone Industries. By A. R. Amos, Jr., and S. B. Patterson. (T.P. 679, with discussion)
Preparation of High-specification Sand at the Grand Coulee Dam. By Anthony Anable. (T.P. 715, with discussion)
A Method for Estimating the Efficiency of Pulverizers. By Raymond Wilson. (T.P. 810)
Metal Consumption in Hammer Mills at Norris Dam. By Francisco Cadena. (T.P. 824, with discussion)
Flotation Processing of Limestone. By Benjamin L. Miller and Charles H. Breerwood. (T.P. 606, with discussion)
Study of the Flotative Properties of Gypsum. By W. E. Keck and Paul Jasberg. (T.P. 762)
Flotation of California Magnesites. By Eric Sinkinson and S. D. Michaelson. (T.P. 733)
Froth Flotation of Southern Barite Ores. By R. G. O'Meara and G. D. Coe. (T.P. 678, with discussion)
Drying and Processing of Pebble Phosphate in the Florida Field. By Charles N. Becker. (T.P. 677, with discussion)
Ore-dressing Practice with Florida Pebble Phosphates, Southern Phosphate Corporation. By J. W. Pamplin
Concentration of Georgia Kyanite Ore. By R. G. O'Meara and B. W. Gandrud. (Contrib. 98, with discussion)

# Principles of Flotation, IV—An Experimental Study of Influence of Sodium Sulfide, Alkalies and Copper Sulfate on Effect of Xanthates at Mineral Surfaces

By Ian William Wark* and Alwyn Birchmore Cox*

(New York Meeting, February, 1936)

Sodium sulfide is used extensively to increase the recovery of oxidized copper and lead minerals by flotation, particularly when using xanthates as collectors. It is generally assumed that the sodium sulfide converts a film of the oxidized mineral to the sulfide, and that the xanthate, while not a very effective collector for the oxidized minerals, is a good collector for the sulfide. On the other hand, Taggart and his collaborators[1] claim that unless sulfide minerals are oxidized they cannot adsorb xanthates and do not float. Gaudin[2] states that amyl xanthate, used in conjunction with sodium sulfide, gives better results than ethyl xanthate. Rabone[3] and Mayer-Schranz[4] agree that excess of sulfide functions as a depressant. Owing to the greater solubilities of the oxidized minerals than of the sulfides, the consumption of sodium sulfide is greater than that of most other flotation reagents, up to 10 lb. per ton of ore being used in some plants. Luyken and Bierbrauer[5] recommend a water washing to remove soluble heavy metal salts; by this means sulfide consumption may be reduced.

It was desirable to determine the limits of the sulfide concentrations between which contact is possible at surfaces of anglesite and cerussite in xanthate solutions. Similar determinations were desirable for the sulfide minerals with which the oxidized minerals are usually associated, since conditions should be chosen, if possible, so that the two types of mineral will float together. Because of the formation, especially in acid solutions, of hydrogen sulfide and of the hydrosulfide ion ($HS^-$), the permissible limits of sulfide addition are obviously dependent upon the pH value. Sphalerite responds to ethyl xanthate only in the presence of an activator; for example, copper sulfate. It was necessary, therefore, to determine whether sodium sulfide interferes with the activation of sphalerite by copper sulfate. The combined effect of sulfide and copper sulfate was determined also for galena, chalcopyrite and pyrite.

---

Manuscript received at the office of the Institute April 25, 1935. Issued as T. P. 659, January, 1936.

* Department of Chemistry, University of Melbourne, Victoria, Australia.

[1] References are at the end of the paper.

In the preceding papers of this series[6,7,8] it has been assumed that the consumption of collectors by the test specimens of sulfide minerals has been negligible. With oxidized minerals such an assumption is invalid, because of the consumption of sodium sulfide and of ethyl xanthate. A method has been developed by which the concentration of sulfide and of xanthate in a given solution can be estimated. Using this method the above assumption that the consumption of xanthates by the sulfide minerals is negligible has been verified.

## EXPERIMENTAL METHODS

### *Contact Measurements*

The principle upon which the work has been based is that contact with an air bubble must be possible for a mineral to float. To determine whether contact is possible the method already described[6] has been used. The procedure in determining the effects of variations in sodium sulfide addition and in pH value has been similar to that adopted[7] in determining the effects of variations in sodium cyanide additions and pH values. The experimental results have been plotted in a similar manner. Using pH value as abscissa and sodium sulfide addition as ordinate, a curve is constructed which separates solution conditions in which air-mineral contact is possible from those in which contact is not possible. Each curve is specific for a particular collector at a given concentration.

Because of the volatility of hydrogen sulfide, the glass cells were kept covered by ground-glass plates and the concentration was checked after most of the tests. Except in acid solutions the loss of sulfide seldom exceeded 2 mg. per liter under these conditions. Aeration removes hydrogen sulfide rapidly from acid or even from slightly alkaline solutions. Consequently control of sulfide concentration would be difficult in practical flotation, except at pH values above 9. Aeration will also tend to oxidize the sulfide; indeed, sulfoxides can be detected after all the sulfide has been lost.

### *Consumption of Reagents*

The estimation of sulfide and xanthate in the same solution is difficult. Taylor and Knoll[9] describe a method for the estimation of thiosulfates and similar sulfoxides in the presence of xanthate. After acidification with tartaric acid any undecomposed xanthic acid is extracted with toluene. The sulfoxide content is then determined by an iodine titration. The xanthate is determined by difference between the sulfoxide titration and a titration on the original solution. However, this method is inapplicable for sulfide because of the volatility of hydrogen sulfide.

An attempt to separate lead xanthate from lead sulfide by solution in alcohol or acetone, followed by titration of the solution of lead xanthate, was unsuccessful. This procedure may give approximately true results with acetone, but a trace of lead xanthate usually remains undissolved, and the acetone, unless specially pure, consumes iodine. Alcohol prevents a sharp end point.

A method depending upon the solubility of lead xanthate and the comparative insolubility of lead sulfide in $N/200$ NaOH proved satisfactory. Titration with $N/1000$ iodine of part of the original solution brought to pH = 8 gives the sum of the sulfide and xanthate concentrations. To a second portion is added sufficient caustic soda to bring the concentration to $N/200$, the sulfide is precipitated by a slight excess of a 5 gram per liter lead acetate solution, and after filtration the filtrate (containing the xanthate) is neutralized and titrated against $N/1000$ iodine. The sulfide is determined by difference. The method fails in the presence of sulfoxides, which behave like the xanthate. A combination of this method and that of Taylor and Knoll might then be satisfactory.

When titrating with dilute iodine solutions, potassium iodide is customarily used to intensify the blue starch iodine coloration, but Taylor and Knoll used potassium sulfate. Excess potassium salts give a violet coloration rather difficult to detect, whereas sodium sulfate gives a blue color; accordingly, 0.5 gram of sodium sulfate was used for each titration, together with 0.5 c.c. of a 5 gram per liter solution of soluble starch. Addition of the sodium sulfate before filtration assisted the coagulation of lead sulfide by shaking. The indicator allowance was directly proportional to the volume and for a total volume of 25 c.c. was approximately 0.25 c.c.; over a wide range it was independent of the amount of sodium sulfate added. The degree of accuracy of the estimation is shown in Table 1; it is least in solutions for which the sulfide to xanthate ratio is highest, the end point of the xanthate titration then

TABLE 1.—*Accuracy of Method of Estimation of Xanthate and Sulfide in Mixed Solutions*

| Solution No. | Xanthate, Mg. per Liter | | Sulfide, Mg. per Liter | |
|---|---|---|---|---|
| | Estimated | Found | Estimated | Found |
| I | 25 | 24<br>26 | 10 | 8<br>9 |
| II | 12.5 | 12.5 | 50 | 48 |
| III | 25 | 25.6<br>25.6 | 25 | 25.0<br>25.2 |
| IV | 25 | 28<br>29 | 100 | 93<br>94 |
| V | 100 | 99<br>100 | 10 | 7.8<br>9.0 |

being somewhat indistinct. All of the tests reported in this paper were carried out at room temperature.

### *Materials*

The xanthates were prepared and purified as previously described[6]; all other materials were of A.R. standard. Large crystals of sodium sulfide ($Na_2S.9H_2O$) were used, the outer surfaces being dissolved initially to remove impurities.

## EXPERIMENTAL RESULTS

### *A. Oxidized Lead Minerals*

*Activation of Anglesite and Cerussite by Sodium Sulfide.*—The relatively high solubilities of anglesite and cerussite lead to the formation, by double decomposition with soluble sulfides and xanthates, of heavy precipitates of lead sulfide and lead xanthate, which are respectively black and white. In a mixed solution, the nature of the precipitate depends upon the composition of the solution; at times it is adherent and protects the surface; at other times it streams away from the surface; sometimes precipitation ceases within an hour—sometimes it continues until no reagents are left in the solution. The color of the precipitate likewise varies with the conditions, but certain broad generalizations are possible for 25 mg. per liter KEtX solutions. The precipitate on cerussite is white in solutions in which the pH value is less than 11 and in which the sulfide concentration* is less than 25 mg. per liter, and varies in color to a deep glossy black in solutions containing 100 mg. per liter of the sulfide. It is not uncommon to have both a black precipitate of lead sulfide on the surface and a white precipitate of lead xanthate streaming from it. The precipitate on anglesite is white for pH values below 11 and sulfide concentrations below 50 mg. per liter but is black if either the sulfide addition or the alkali addition is increased; i.e., if the sulfide-ion concentration is increased. The deposits are most adherent in the pH region of 8 to 10.

Since surface precipitates hinder contact with an air bubble, the characteristic angles for ethyl and isoamyl xanthates, 60° and 86° respectively, are seldom attained in full, and the determination of contact curves is more difficult than usual. In many cases contact is possible only after the surface precipitate has been removed by the routine procedure[7] of wiping the surface with linen. At times the precipitate may adhere to an air bubble; at other times, however, it may not do so even when the surface, after being freed from it, is air-avid.

The effect of xanthate alone had first to be investigated. Fig. 1 shows the manner in which the concentration of ethyl xanthate necessary to induce air-mineral contact depends upon the pH value. With anglesite, contact is most readily induced between the pH values 9.5 and 11; the concentration of xanthate can be reduced to below 50 mg. per liter within this range. Below 9.5 there is a gradual increase, and above 11 there is a rapid increase in the concentration of xanthate necessary to induce contact. The consumption of xanthate is lowest within this optimum range. Above 11, if insufficient xanthate is available to protect it, the surface becomes etched by the alkali. With cerussite, however, contact is induced by 50 mg. per liter potassium ethyl xanthate at pH values below 9. In more alkaline solutions, the concentration of the xanthate must be increased rapidly as the pH value rises.

---

* Concentrations of sulfide cited throughout this paper are for $Na_2S.9H_2O$.

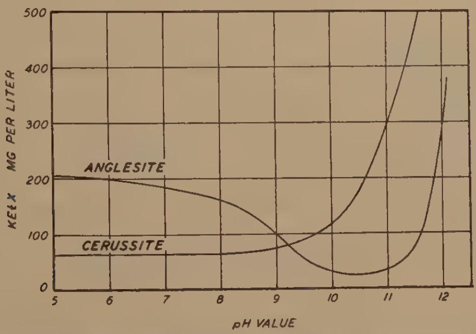


FIG. 1.—RELATIONSHIP BETWEEN pH VALUE AND CONCENTRATION OF POTASSIUM ETHYL XANTHATE NECESSARY TO INDUCE CONTACT AT SURFACES OF ANGLESITE AND CERUSSITE (CARBONATE-FREE SOLUTIONS).

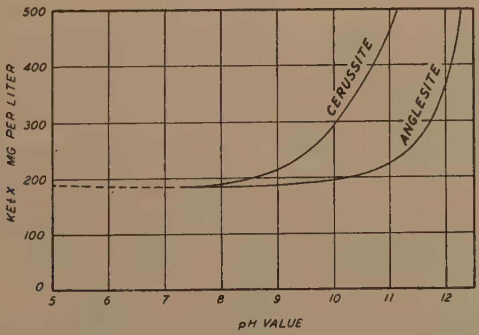


FIG. 2.—CONCENTRATION OF POTASSIUM ETHYL XANTHATE NECESSARY TO INDUCE CONTACT WITH SURFACES OF ANGLESITE AND CERUSSITE.

$Na_2CO_3$ = 250 mg. per liter.

Lead carbonate being less soluble than lead sulfate, sodium carbonate may be expected to influence the response of anglesite to xanthates. Sodium carbonate was not used, therefore, in determining the curves of Fig. 1, caustic soda being used instead. The influence of 250 mg. per liter of sodium carbonate on the position of these curves is shown in Fig. 2.

With both minerals, carbonate increases the amount of xanthate necessary to induce contact. This effect is not due to the change in pH value produced by the carbonate and can be attributed only to the carbonate or bicarbonate ion.

One might anticipate that the addition of sodium sulfate would have a similar effect on anglesite, but 300 mg. per liter $Na_2SO_4$ is without influence on the curve of Fig. 1. Addition of sulfate does, however, appear to lessen the consumption of xanthate, and therefore may slightly increase its effective concentration.

Fig. 3 shows how the addition of sodium sulfide induces contact between the surface of anglesite and an air bubble in solutions containing 25 mg. per liter potassium ethyl xanthate and 31.6 mg. per liter potassium amyl xanthate respectively. (These concentrations are chemically equivalent.) However if, as in the right-hand portion of the diagram, the concentration of sulfide or alkali is too great, contact is not possible. On the left of the diagram, there is a second region where contact is impossible: in such acid solutions the sulfide-ion concentration is not sufficiently high to activate the anglesite. In Fig. 4 are given the corresponding curves for cerussite.

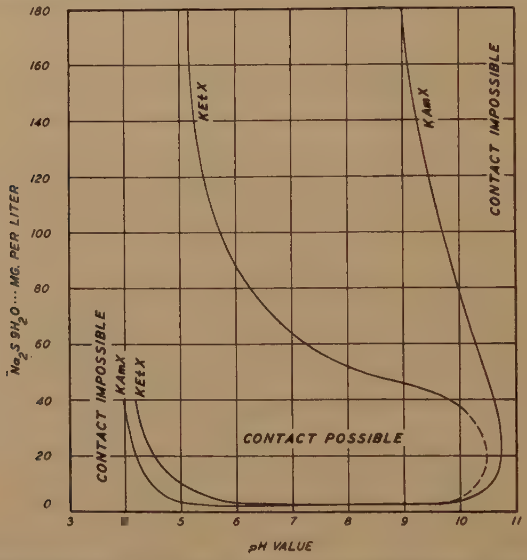


Fig. 3.—Influence of pH value and of concentration of sodium sulfide on contact at a surface of anglesite. (Contact possible to left of curve except as indicated.)

KEtX = 25 mg. per liter. KAmX = 31.6 mg. per liter.

*Consecutive Treatment by Sulfide and Xanthate.*—Sometimes more can be learned of the functions of flotation reagents by allowing them to react singly on the mineral than by studying the response of the mineral to the simultaneous action of more than one reagent. Cerussite was placed for 30 min. in a 100 mg. per liter $Na_2S.9H_2O$ solution at a pH value of 8. It was then washed and placed in a 25 mg. per liter KEtX solution. On wiping the surface, the contact angle was 57°. Omitting the initial sulfide treatment, only irregular and partial contact could be obtained. Considerably more xanthate (see Fig. 1) is necessary to induce full contact in the absence of sulfide.

Similar tests with anglesite did not lead to a definite conclusion. Though prior treatment with sodium sulfide slightly improved the response to ethyl xanthate, the formation of a heavy precipitate prevented good contact.

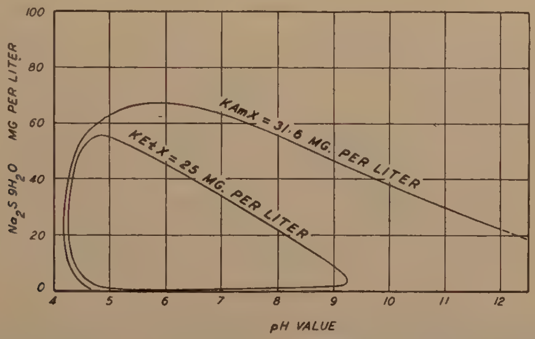


Fig. 4.—Influence of pH value and of concentration of sodium sulfide on contact at a surface of cerussite. (Contact possible inside curves.) KEtX = 25 mg. per liter. KAmX = 31.6 mg. per liter.

### *B. Sulfide Minerals*

Results for galena, pyrite, activated sphalerite and four copper-bearing minerals are presented in Fig. 5, the collector being 25 mg. per liter KEtX. The sphalerite was activated by immersion in a solution of copper sulfate and was washed before testing. The curve for this mineral, therefore, shows the amount of sodium sulfide necessary to overcome accidental activation of the sphalerite by copper salts. The determination of these curves was more difficult than the corresponding cyanide curves[7,8]. If the sulfide concentration is only slightly below the critical concentration that prevents contact, wiping by linen is necessary. Indeed, the full characteristic angle of contact for ethyl xanthate is seldom obtained close to the curves.

An increase in the xanthate concentration to 625 mg. per liter has very little influence on the position of the curve for galena. It may be assumed that the position of the curves for the other minerals would be altered only slightly by an increase in the xanthate concentration.

*Influence of Copper Sulfate.*—Copper sulfate, which reacts with both sulfides and alkalis, alters the positions of the curves. The lowest curve of Fig. 6 shows the relationship between the pH value and the quantity of sodium sulfide necessary to prevent air-contact at a sphalerite surface, the concentration of KEtX being 25 mg. per liter and that of copper sulfate 150 mg. per liter. Consecutive tests show that activation of the sphalerite occurs equally well whether xanthate is present or not,

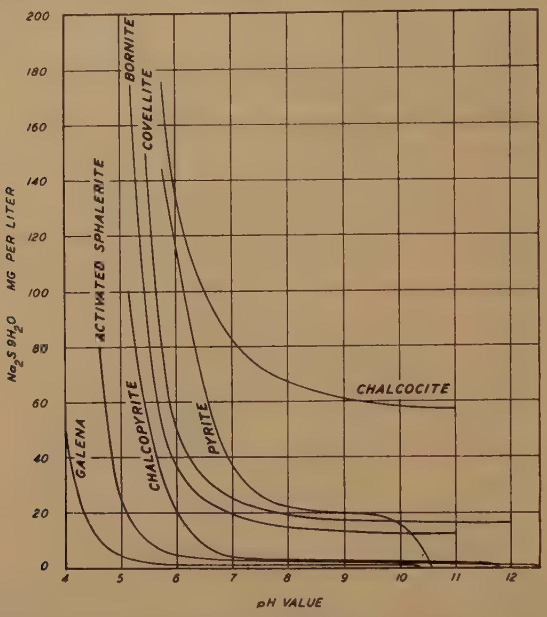


FIG. 5.—RELATIONSHIP BETWEEN pH VALUE AND CONCENTRATION OF SODIUM SULFIDE NECESSARY TO PREVENT CONTACT AT SURFACES OF VARIOUS SULFIDE MINERALS.

KEtX = 25 mg. per liter.

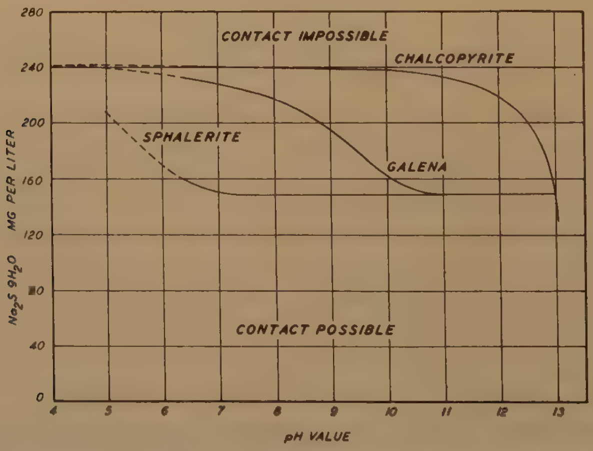


FIG. 6.—INFLUENCE OF SODIUM SULFIDE CONCENTRATION AND OF pH VALUE ON CONTACT AT MINERAL SURFACES IN PRESENCE OF 150 MG. PER LITER OF $CuSO_4.5H_2O$.

KEtX = 25 mg. per liter.

but for contact to occur xanthate must be present. The curves for galena and chalcopyrite are also shown in Fig. 6. The corresponding curve (Fig. 7) for pyrite in the presence of 25 mg. per liter KEtX, differs markedly from any curve previously determined. With 150 mg. per liter $CuSO_4.5H_2O$ present, up to 20 mg. per liter $Na_2S.9H_2O$ does not prevent contact with an air bubble. There is an intermediate range of sulfide concentration, dependent upon the pH value, where contact is difficult to establish and the angle of contact is irregular and less than 60°. Above this region is a broader one where no contact is possible; similarly, at pH values above 13, contact ceases to be possible, whatever the sulfide concentration. Just below 144 mg. per liter $Na_2S.9H_2O$ (which is the stoichiometric equivalent of the copper sulfate) contact again becomes possible and the full angle of 60° is reached; this second region of contact extends up only to between 300 and 400 mg. per liter. At pH values lower than 6, contact is possible at any sulfide concentration below 400 mg. per liter.

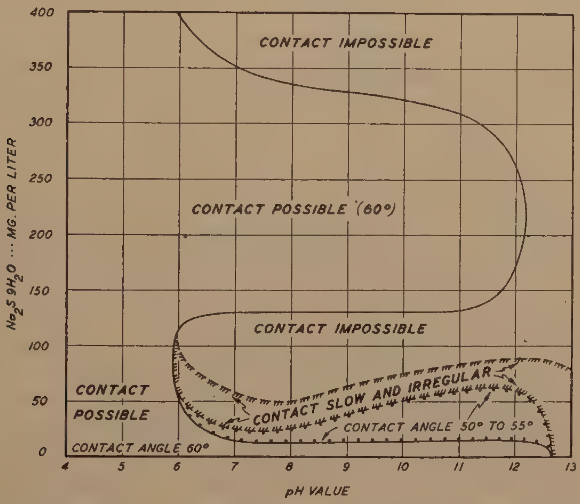


FIG. 7.—INFLUENCE OF SODIUM SULFIDE CONCENTRATION AND OF pH VALUE ON CONTACT AT A SURFACE OF PYRITE IN PRESENCE OF 150 MG. PER LITER OF $CuSO_4.5H_2O$.

KEtX = 25 mg. per liter.

### *C. Consumption of Xanthate and Sulfide*

*Xanthate Alone.*—Single specimens of the minerals were placed in 35 c.c. of the xanthate solution, the concentration of the solution being determined at the time of introduction and again after contact for 30 min. or longer. The surface area of each specimen was approximately 8 sq. cm. A control test was carried out to determine whether there was loss of xanthate from decomposition as distinct from consumption.

Siedler[10] and Knoll[11] have shown that potassium ethyl xanthate is stable in neutral or alkaline solution. Table 2 shows the rate of decomposition in an acid solution under the conditions of experiment. The initial pH value was 4.7. The progressive decrease in the rate of decomposition is due to a gradual increase in pH value, alkali being a decomposition product.

TABLE 2.—*Rate of Decomposition of Ethyl Xanthate in Acid Solution*

| Time | Titration, C.c. *N*/1000 Iodine | pH Value | KEtX, Mg. per Liter |
|---|---|---|---|
| 5 min | 4.28 c.c. | 4.7 | 27 |
| 25 min | 4.13 | 4.9 | 26 |
| 60 min | 3.83 | 5.3 | 24.5 |
| 90 min | 3.63 | 5.4 | 23 |
| 120 min | 3.55 | 5.4 | 22.5 |
| 18 hr | 2.90 | 6.3 | 18.5 |

Table 3 records the consumption of xanthate by several minerals for periods of immersion from 30 to 90 min. The pH value was between 6 and 7 in all cases. Only with anglesite was there a rapid though very variable consumption of xanthate.

TABLE 3.—*Consumption of Ethyl Xanthate by Various Minerals*

| Test | Initial KEtX, Mg. per Liter | Time of Test, Min. | Final KEtX, Mg. per Liter | | | | |
|---|---|---|---|---|---|---|---|
| | | | Control | Galena | Chalcopyrite | Cerussite | Anglesite |
| 1 | 25.0 | 30 | 24 | 22 | | | 18 |
| 2 | 25.0 | 90 | | 25 | | | 1.5 |
| 3 | 25.6 | 60 | 25.6 | | 25.6 | 23.7 | |
| 4 | 25.0 | 60 | 24.3 | | | 23.7 | 20.4 |

TABLE 4.—*Consumption of Sodium Sulfide by Various Minerals*

| Test | pH Value | Initial $Na_2S.9H_2O$, Mg. per Liter | Time of Test, Min. | Final $Na_2S.9H_2O$, Mg. per Liter | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | Control | Galena | Chalcopyrite | Cerussite | Anglesite |
| 1 | 4.4 | 14 | 60 | 12 | 12 | | | |
| 2 | 6.8 | 7 | 60 | 6 | 6 | 6 | | |
| 3 | 7.2 | 26 | 60 | 26 | 25 | | | 16 |
| 4 | 7.2 | 36 | 120 | 32 | | | 26 | 24 |
| 5 | 7.2 | 36 | 60 | 31 | | | 27 | 24 |
| 6 | 9.1 | 25 | 45 | 24 | 23 | | | 21 |
| 7 | 9.2 | 36 | 60 | 35 | | | 32 | 24 |
| 8 | 9.2 | 33 | 30 | 33 | 33 | 34 | | |

*Sulfide Alone.*—A similar series of tests was designed to determine the consumption of sulfide under precisely similar conditions with regard to solution volume and size of specimens. Various pH values were tested, as shown in Table 4.

*Xanthate and Sulfide Both Present.*—The tests were conducted in the same manner, but because of the necessity for two titrations a larger volume of solution, 45 c.c., was taken. For an initial pH value of 7, and various ratios of sulfide to xanthate, Table 5 records the consumption of reagents by galena, anglesite and cerussite. Some sulfide was probably lost by volatilization of hydrogen sulfide.

TABLE 5.—*Consumption of Xanthate and Sulfide by Lead Minerals*

| Test No. | Initial Concentrations, Mg. per Liter | | Time of Test, Min. | Final Concentration | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Control | | Galena | | Anglesite | | Cerussite | |
| | KEtX | $Na_2S.9H_2O$ | | KEtX | $Na_2S.9H_2O$ | KEtX | $Na_2S.9H_2O$ | KEtX | $Na_2S.9H_2O$ | KEtX | $Na_2S.9H_2O$ |
| 1 | 12.5 | 36 | 60 | 12.5 | 33 | 14 | 36 | 13 | 22 | | |
| 2 | 12.5 | 38 | 120 | 12 | 34 | 13 | 27 | 14 | 8 | | |
| 3 | 23 | 45 | 150 | 21 | 44 | 22 | 33 | 21 | 23 | | |
| 4 | 26 | 25 | 90 | 26 | 21 | | | 26 | 12 | 27 | 12 |

The results of an attempt to determine the effect of variations in pH value are shown in Table 6.

TABLE 6.—*Effect of pH Value on Consumption of Reagents by Lead Minerals*

| Test No. | pH Value (Initial) | Initial Concentrations | | Time of Test, Min. | Final Concentrations | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Control | | Anglesite | | Cerussite | |
| | | KEtX | $Na_2S.9H_2O$ | | KEtX | $Na_2S.9H_2O$ | KEtX | $Na_2S.9H_2O$ | KEtX | $Na_2S.9H_2O$ |
| 1 | 5.2 | 24 | 17 | 90 | 10 | 14 | 2 | 5.5 | 18 | 11 |
| 2 | 6.9 | 26 | 25 | 90 | 26 | 21 | 26 | 12 | 27 | 12 |
| 3 | 9.2 | 26 | 24 | 90 | 27 | 25 | 25 | 18 | 28 | 21 |
| 4 | 11.0 | 26 | 26 | 90 | 24 | 26 | 25 | 10 | 26 | 21 |

Evidently in acid solutions the rates of decomposition of the xanthate and of volatilization of hydrogen sulfide are not sufficiently controlled, but in alkaline solutions the results indicate that anglesite and cerussite consume appreciable amounts of sulfide in preference to xanthate. This is confirmed by marked blackening of the specimens. The sulfide consumption is very irregular, however, and probably depends to some extent on the specimen. Consumption of reagents by finely ground minerals must be very high.

## Discussion of Results

### A. *Anglesite and Cerussite*

The response of cerussite to consecutive treatment by sulfide and xanthate supports the suggestion that its activation is due to the formation of a film of lead sulfide. The depressant action of an excess of sulfide on this film is more difficult to explain. Even allowing for a very high consumption of sulfide, a higher sodium sulfide concentration can apparently be tolerated by activated cerussite than by galena. This may be due to the generation by the activation process of a film of lower than average sulfide concentration near the cerussite surface. It is known that diffusion may be extremely slow near the surface of a solid.

The curves of Figs. 3 and 4 are difficult to interpret. Probably the right-hand portions of the anglesite curves of Fig. 3 should be regarded as corresponding with the curves of Fig. 5 for the sulfide minerals. The lower left-hand portion of the curve divides the region in which there is sufficient sulfide available for the activation of the anglesite from the region (below the curve) where there is insufficient. The prevention of contact beyond the extreme right-hand portion should probably be regarded as due directly to alkali. Thus it is necessary to have a certain minimum concentration of sulfide to activate the anglesite, but excess of sulfide prevents contact by the same process as obtains for the sulfide minerals, and, as always, excess of alkali also prevents contact. The cerussite curves can be interpreted similarly, but there is another important factor, the decomposition of xanthate, which leads to a diminution (in acid solutions) of the amount of sulfide necessary to prevent contact. The curves therefore become closed at the top left-hand portion of the diagram. Test I of Table 6 shows how important decomposition of xanthate may become.

Though sodium sulfide has proved satisfactory on the large scale for cerussite, it is not ideal for anglesite. Some results with sodium hydrogen phosphate are illuminating, and it may prove to be a suitable activator for anglesite. When using amyl xanthate as a collector, up to at least one gram per liter of the phosphate does not prevent contact at surfaces of galena and (activated) sphalerite. It has the disadvantage, however, that anglesite itself can tolerate less excess than of sulfide. The position, therefore, is that sodium phosphate is a safer reagent than sodium sulfide for the sulfide minerals, but does not allow as great latitude with anglesite. However, its concentration should be more easily controlled than that of the sulfide. Direct flotation tests are needed to ascertain whether phosphate can be substituted for sulfide with advantage in practice.

A curve for anglesite with amyl xanthate as collector and sodium phosphate as activator is shown in Fig. 8.

Sodium phosphate was selected for trial because lead phosphate is relatively insoluble. It is, in fact, stated to be less soluble than lead sulfide, but little credence can be given to reported solubilities of such slightly soluble compounds. Trial as activators of other anions that form highly insoluble salts with lead might be profitable.

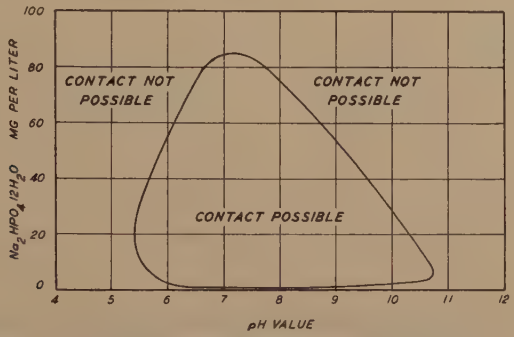


FIG. 8.—INFLUENCE OF SODIUM PHOSPHATE CONCENTRATION AND OF pH VALUE ON CONTACT AT A SURFACE OF ANGLESITE.

KAmX = 31.6 mg. per liter.

## *B. Sulfide Minerals*

The results for sodium sulfide and sodium cyanide are very similar. Sodium sulfide, however, can prevent contact at galena surfaces, whereas sodium cyanide does not; furthermore, of the sulfide minerals tested pyrite, which required least cyanide, requires almost as much sulfide as does chalcocite to prevent contact at its surface.

Like hydrocyanic acid, hydrogen sulfide is a weak acid. It differs from hydrocyanic acid, however, in being dibasic. Both acids are converted completely to ionized salts in strongly alkaline solutions and are incompletely ionized in neutral or acid solutions. In neutral or acid solutions, therefore, there is a lower percentage of sulfide ($S^{--}$) and hydrosulfide ($HS^-$) ions than in alkaline solutions. A greater concentration of total sulfide would therefore have to be added to prevent contact in neutral solutions, if either of these ions is responsible for the prevention of contact.

From Landolt-Bornstein Tables [Jellinek Czerwinski: *Ztsch. phys. Chem.* (1922) **102,** 438] at 0° C.,

$$K_1 = \frac{(H^+)(HS^-)}{-(H_2S)} = 10^{-7}$$

$$K_2 = \frac{(H^+)(S^{--})}{-(HS^-)} = 2 \times 10^{-15}$$

Over a wide range of pH values, Table 7 shows the equilibrium concentrations, calculated from the above equations, of hydrogen sulfide, hydrosulfide ion and sulfide ion. It will be seen that the concentration of sulfide ion is always exceedingly small.

TABLE 7.—*Influence of pH Value on Conversion of Sodium Sulfide to Sulfide Ion, Hydrosulfide Ion and Hydrogen Sulfide*

| pH Value | For every milligram $Na_2S.9H_2O$ added per liter there is present as: | | |
|---|---|---|---|
| | $H_2S$, Mg. per Liter | $HS^-$, Mg. per Liter | $S^{--}$, Mg. per Liter |
| 4.0 | 0.142 | 0.00014 | $2.7 \times 10^{-15}$ |
| 4.5 | 0.142 | 0.00042 | $2.7 \times 10^{-14}$ |
| 5.0 | 0.141 | 0.0014 | $2.7 \times 10^{-13}$ |
| 5.5 | 0.138 | 0.0042 | $2.7 \times 10^{-12}$ |
| 6.0 | 0.129 | 0.012 | $2.7 \times 10^{-11}$ |
| 6.5 | 0.106 | 0.034 | $2.1 \times 10^{-10}$ |
| 7.0 | 0.071 | 0.069 | $1.3 \times 10^{-9}$ |
| 7.5 | 0.033 | 0.103 | $8.6 \times 10^{-9}$ |
| 8.0 | 0.013 | 0.124 | $2.6 \times 10^{-8}$ |
| 8.5 | 0.0042 | 0.133 | $9.3 \times 10^{-8}$ |
| 9.0 | 0.0014 | 0.137 | $2.6 \times 10^{-7}$ |
| 10.0 | 0.00014 | 0.137 | $2.6 \times 10^{-6}$ |
| 11.0 | 0.000014 | 0.137 | $2.6 \times 10^{-5}$ |
| 12.0 | 0.0000014 | 0.137 | $2.6 \times 10^{-4}$ |

The curves of Fig. 5 record, for each mineral, the values of the concentration of sodium sulfide just necessary to prevent contact over a range of pH values. By selecting a number of points along each of these lines a number of corresponding values of concentrations of sodium sulfide and hydrogen ion may therefore be obtained for each mineral. Using Table 8, it is then possible to calculate the values of the concen-

TABLE 8.—*Concentrations of Sulfide Ion, Hydrosulfide Ion and Hydrogen Sulfide in Solutions Containing Just Sufficient Total Sulfide to Prevent Contact at a Chalcopyrite Surface*

| pH Value | Total Sulfide as $Na_2S.9H_2O$, Mg. per Liter | $H_2S$, Mg. per Liter | $HS^-$, Mg. per Liter | $S^{--}$, Mg. per Liter |
|---|---|---|---|---|
| 5.0 | 150 | 21 | 0.21 | $4 \times 10^{-11}$ |
| 5.5 | 52 | 7.2 | 0.22 | $1.4 \times 10^{-10}$ |
| 6.0 | 21 | 2.7 | 0.25 | $6 \times 10^{-10}$ |
| 6.5 | 8 | 0.8 | 0.27 | $1.7 \times 10^{-9}$ |
| 7.0 | 4 | 0.3 | 0.28 | $5.2 \times 10^{-9}$ |
| 8.0 | 3 | 0.04 | 0.37 | $7.8 \times 10^{-8}$ |
| 9.0 | 3 | 0.004 | 0.41 | $7.8 \times 10^{-7}$ |
| 10.0 | 2.5 | 0.00035 | 0.34 | $6.5 \times 10^{-6}$ |
| 11.0 | 2.5 | 0.000035 | 0.34 | $6.5 \times 10^{-5}$ |

trations of hydrogen sulfide, hydrosulfide ion and sulfide ion that are present when just sufficient sodium sulfide has been added to prevent contact. Table 8 shows the results of these calculations for chalcopyrite.

There is a very large variation in the concentrations, both of hydrogen sulfide and of sulfide ion along the curve; therefore neither can be the controlling factor with regard to prevention of contact. On the other hand, the variation in the calculated concentration of hydrosulfide ion is probably within the limit of experimental error.* There is evidently what might be called a "*critical hydrosulfide-ion concentration*" below which contact is possible and above which contact is impossible. This critical value depends upon the nature and concentration of the collector.

TABLE 9.—*Concentration of Hydrosulfide Ion in Solutions Containing Just Sufficient Total Sulfide to Prevent Contact at Mineral Surfaces*

| Galena | | | Bornite | | | Covellite | | | Pyrite | | | Chalcocite | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| pH Value | $Na_2S.9H_2O$ Added, Mg. per Liter | $HS^-$, Mg. per Liter Calc. | pH Value | $Na_2S.9H_2O$ Added, Mg. per Liter | $HS^-$, Mg. per Liter, Calc. | pH Value | $Na_2S.9H_2O$ Added, Mg. per Liter | $HS^-$, Mg. per Liter Calc. | pH Value | $Na_2S.9H_2O$ Added, Mg. per Liter | $HS^-$, Mg. per Liter Calc. | pH Value | $Na_2S.9H_2O$ Added, Mg. per Liter | $HS^-$, Mg. per Liter Calc. |
| 4.0 | 50 | 0.007 | 5.5 | 88 | 0.37 | 5.5 | 150 | 0.63 | 6.0 | 115 | 1.38 | 6.0 | 137 | 1.6 |
| 4.5 | 13 | 0.005 | 6.0 | 37 | 0.44 | 6.0 | 50 | 0.60 | 6.5 | 67 | 2.28 | 6.5 | 100 | 3.4 |
| 5.0 | 4 | 0.006 | 6.5 | 25 | 0.85 | 6.5 | 33 | 1.12 | 7.0 | 38 | 2.62 | 7.0 | 83 | 5.7 |
| 5.5 | 2.5 | 0.011 | 7.0 | 19 | 1.31 | 7.0 | 25 | 1.72 | 7.5 | 27 | 2.78 | 7.5 | 73 | 7.5 |
| 6.0 | 1.5 | 0.018 | 7.5 | 17 | 1.75 | 7.5 | 21 | 2.13 | 8.0 | 23 | 2.86 | 8.0 | 67 | 8.3 |
| 7.0 | 1.0(?) | 0.06(?) | 8.0 | 15 | 1.86 | 8.0 | 19 | 2.36 | 8.5 | 21 | 2.80 | 9.0 | 61 | 8.4 |
| 8.0 | ? | ? | 9.0 | 13 | 1.78 | 9.0 | 17 | 2.33 | 9.0 | 20 | 2.74 | 10.0 | 59 | 8.1 |
| | | | 10.0 | 12.5 | 1.71 | 10.0 | 17 | 2.33 | | | | 11.0 | 58 | 7.9 |
| | | | 11.0 | 12.5 | 1.71 | 11.0 | 16 | 2.20 | | | | | | |
| Mean | | (0.01) | | | 1.3 | | | 1.7 | | | 2.5 | | | 6.4 |

Table 9 records similar calculations of the hydrosulfide-ion concentration for the other sulfide minerals. Approximate values of the critical concentration are 0.01 for galena, 0.30 for chalcopyrite, 1.3 for bornite, 1.7 for covellite, 2.5 for pyrite and 6.4 for chalcocite. Though the variation from constancy may appear excessive in some cases, an exceedingly small variation in the slope of the left-hand side of the curves would be sufficient to prevent the falling away in the calculated $HS^-$ concentrations at the top of the column. Below the critical pH value the function of the alkali or acid is evidently merely to control the concentration of the hydrosulfide ion, just as it was shown[7] that alkali merely controlled the cyanide-ion concentration. In both cases, however, if the critical pH value is exceeded, the alkali itself becomes the active depressant.

---

* Absolute constancy cannot be expected. Apart from the difficulties of determining the position of the curve, the dissociation constant of hydrogen sulfide is known only approximately at 0°, and a further error is introduced by accepting the same value for room temperature.

*Influence of Copper Sulfate.*—Qualitatively, except for pyrite, the observed effects of copper sulfate can be attributed to its acting simply as a precipitant for sodium sulfide. For sphalerite between pH values of 7 and 13, the amount of sodium sulfide necessary to prevent contact (between 140 and 150 mg. per liter) is approximately equal to the amount (144 mg. per liter) necessary to completely precipitate the added copper. In this case the explanation is obvious; namely, that activation is possible provided insufficient sulfide has been added to precipitate all the copper; the curve is an activation curve. With the other minerals of Fig. 6, in addition to 144 mg. per liter precipitated by the copper sulfate, an excess of sodium sulfide sufficient to prevent contact with the mineral must be added. It is surprising that such a large excess of sulfide is required (see Fig. 5). Perhaps the explanation lies in the conversion by copper of the surfaces of galena and chalcopyrite to surfaces resembling covellite or chalcocite. The results of Fig. 7 for pyrite cannot be interpreted in terms of these considerations.

### *C. Consumption of Reagents*

Under the conditions that these "captive-bubble" tests are carried out, the sulfide minerals consume an inappreciable amount of xanthate or sulfide. Even cerussite consumes so little that the concentration of the solution is not reduced greatly, though visible changes occur at the surface. Under some conditions, however, anglesite may continue to react until the concentration of xanthate or of sulfide is decreased considerably.

When both sulfide and xanthate are present, the former is consumed in preference to the latter. This is presumably due to a lesser solubility of lead sulfide. The film of lead sulfide that is formed evidently prevents rapid interaction between anglesite and potassium xanthate.

## SUMMARY

The influence of sodium sulfide on the contact induced by xanthate between an air bubble and the minerals anglesite, cerussite, galena, sphalerite, pyrite, chalcopyrite, bornite, covellite and chalcocite has been investigated. It has been shown that:

1. Sodium sulfide is a depressant for the sulfide minerals.
2. The concentration of sodium sulfide necessary to prevent contact is a function of the pH value.
3. The hydrosulfide ion ($HS^-$) is the effective depressant and there is, for each mineral, a critical hydrosulfide-ion concentration just sufficient to prevent response to a given concentration of potassium ethyl xanthate. This critical value is not greatly influenced by the xanthate concentration.

4. Copper sulfate influences the effect of sodium sulfide on galena and chalcopyrite, probably removing it from solution as a precipitate of cupric sulfide.

5. Copper sulfate must be stoichiometrically in excess of the sulfide if it is to activate sphalerite.

6. The combined influence of copper sulfate and sodium sulfide on pyrite is exceedingly complex.

7. The concentration of potassium ethyl xanthate necessary to induce contact between an air bubble and anglesite and cerussite respectively has been investigated as a function of pH value. Anglesite responds most readily between the pH values of 9 and 11, cerussite at pH values below 9.

8. Sodium carbonate increases the concentration of ethyl xanthate necessary to induce a response at surfaces of anglesite and cerussite.

9. Controlled concentrations of sodium sulfide activate anglesite and cerussite so that they respond to lower concentrations of xanthate, but excess of sulfide prevents a response.

10. Cerussite responds more readily to xanthate after an initial treatment with sodium sulfide. It is argued that this activation is due to the formation of a surface film of lead sulfide. There is a corresponding blackening of the surface.

11. The response of anglesite and cerussite to amyl xanthate is less influenced by sodium sulfide than their response to ethyl xanthate.

12. Sodium phosphate may be substituted for sodium sulfide as an activator for anglesite and cerussite.

13. A method has been developed for the estimation of xanthate and sulfide in a single solution and their consumption by test specimens of the minerals has been investigated.

14. The test specimens of sulfide minerals consume very little sulfide or xanthate, but cerussite may consume appreciable amounts. Under some conditions anglesite may consume a considerable fraction of the xanthate present.

15. Sulfide is consumed in preference to xanthate by anglesite and cerussite.

16. Because of the volatility of hydrogen sulfide and the readiness with which sodium sulfide is oxidized it would be difficult to control the sulfide concentration of flotation-plant circuits.

## ACKNOWLEDGMENTS

The authors desire gratefully to acknowledge the encouragement and help they have received from the companies for which the work has been carried out: Broken Hill South Ltd., North Broken Hill Ltd., Zinc Corporation Ltd., Electrolytic Zinc Co. of Australasia Ltd., Mount Lyell Mining and Railway Co. Ltd., and the Burma Corporation Ltd.

To Mr. Hey, under whose general direction the work has been carried out, they are especially indebted. Prof. E. J. Hartung has generously provided laboratory accommodation for the research in the Chemistry Department of the University of Melbourne.

## REFERENCES

1. A. F. Taggart, T. C. Taylor, and A. F. Knoll: Chemical Reactions in Flotation. *Trans.* A.I.M.E. (1930) **87**, Milling Methods, 247.
2. A. M. Gaudin: Flotation, 301. New York, 1932.
3. P. Rabone: Flotation Plant Practice, 75. London, 1932.
4. E. W. Mayer and H. Schranz: Flotation, 279. Leipzig, 1931.
5. W. Luyken and E. Bierbrauer: Die Flotation in Theorie und Praxis, 201. Berlin, 1931.
6. I. W. Wark and A. B. Cox: *Trans.* A.I.M.E. (1934) **112**, 189.
7. I. W. Wark and A. B. Cox: *Trans.* A.I.M.E. (1934) **112**, 245.
8. I. W. Wark and A. B. Cox: *Trans.* A.I.M.E. (1934) **112**, 267.
9. T. C. Taylor and A. F. Knoll: *Trans.* A.I.M.E. (1934) **112**, 382.
10. P. Siedler: *Met. u. Erz* (1931) **28**, 425.
11. A. F. Knoll: Thesis, Columbia University, 1932.

## DISCUSSION

(*Arthur F. Taggart presiding*)

M. REY,* Liége, Belgium (written discussion).—The authors refrain from giving any interpretation of their results, perhaps because they do not want to commit themselves to any theory. However, it seems to me that their findings can receive the following tentative interpretation in terms of the chemical theory of flotation.

According to the chemical theory, the collecting action of xanthates is due to a chemical reaction between the xanthate anion and metallic cations existing at the surface of the mineral. It follows that the control of the concentration of these cations is essential to flotation.

At the surface of oxidized relatively soluble minerals like anglesite or cerussite, the concentration of metallic ions is necessarily high. According to Luyken and Bierbrauer,[12] they form a cloud around the mineral, which precipitates the ions of the collector and prevents them from approaching the mineral surface. In this way, a small concentration of xanthate forms with these minerals a visible and useless xanthate precipitate instead of the useful, invisible and oriented film. Similarly, it can be shown that whereas a small concentration of a mercuric salt activates sphalerite and permits its flotation with xanthate, a high concentration prevents flotation, unless the concentration of xanthate is proportionally raised. Apparently the function of sodium sulphide or sodium phosphate is to precipitate this cloud or to reduce this concentration. From a state of "overactivation," the mineral is brought to a state of correct activation similar to that which exists naturally at the surface of galena in aerated water. The authors show that the concentration of sodium sulphide necessary for this work is higher with anglesite than with cerussite, which is in accord with the greater solubility of anglesite.

The depressing effect of an excess of sodium sulphide or phosphate is apparently due to the complete neutralization of the lead cations with the formation of lead sulphide or phosphate. This might well be termed "de-activation." The concentration of sodium sulphide or, as the authors show, of $HS^-$ ion necessary to cause this deactivation increases in the order: galena, cerussite, anglesite, which is the order of increasing lead cation concentration. In other words, the stronger the activation, the greater the sulphide concentration necessary to cause deactivation.

---

* Professor of Nonferrous Metallurgy, University of Liége.

[12] Die Flotation in Theorie und Praxis, 38. Berlin, 1931.

The fact that chalcocite is very difficult to depress with sodium sulphide can also apparently be traced to the relatively strong state of activation of this mineral, which is well known to be a ready source of copper ions.

If the above interpretation is correct, it would appear preferable not to use the term "activation" for the action of sodium sulphide on anglesite and cerussite.

# Principles of Flotation, V—Conception of Adsorption Applied to Flotation Reagents

By Ian William Wark* and Alwyn B. Cox*

(New York Meeting, February, 1937)

In defending the chemical theory of flotation, Taggart, del Giudice and Ziehl have criticized[1] the views of those who prefer to attribute the effects of certain flotation agents to adsorption. Perhaps with some justification, they describe the latter term as the "haven of refuge of writers lost in a morass of shaky experiment and muddy thinking." We prefer to regard it, however, as a haven of refuge for writers who seek a conventional term to describe the formation of films of flotation reagents on solid surfaces, because in many cases it is not yet possible to specify the forces that hold them there.

Originally, as Taggart and his associates state, adsorption connoted a concentration difference and nothing more. In recent years, workers in the field of surface chemistry have tacitly added other meanings, and they now speak of orientated adsorption of unimolecular films on a solid substrate, of chemi-adsorption, and of exchange adsorption. Thus the term adsorption may connote simply the Gibbs layer of excess concentration at the surface of a solution, or a unimolecular film at the surface of a solid. Perhaps this has led to the misunderstanding of Taggart, del Giudice and Ziehl concerning the relationship between surface tension and adsorption at solid surfaces. The change in "surface tension" accompanying adsorption at a liquid surface can be used as a measure of the adsorption, and the Gibbs equation as quoted by these authors correlates these two conceptions. But, to correlate two conceptions does not necessarily imply an attempt to explain either, although sometimes such an "explanation" is carelessly inferred. Use of "surface energy per unit area" instead of the numerically equal but more difficult and less definite conception of "surface tension per unit length" would lessen many of the present difficulties. (Compare with Adam.[2]) At interfaces involving a solid phase, neither "surface tension" nor "interfacial tension" can have any meaning, but the conception "interfacial energy per unit area" can be understood by anyone who is familiar with the concept of free energy. While it is true that surface energy cannot be directly measured at a solid surface,

---

Manuscript received at the office of the Institute April 10, 1936. Issued as T. P. 732, September, 1936.

* Flotation Research Laboratory, Department of Chemistry, University of Melbourne, Melbourne, Australia.

[1] References are at the end of the paper.

there is abundant evidence that the interfacial energy of a mineral surface depends upon the solution with which it is in contact. The angle of contact in a dilute solution of any common collector is determined primarily by the difference between the interfacial energy of the mineral-air and mineral-water interfaces: consequently, when xanthate changes the angle of contact it has necessarily changed these interfacial energies also. Thus it is not correct to imply that those who do not accept the Taggart hypothesis base their explanation on "an assumption of surface tension changes at an interface (liquid-solid) at which no definite determination of even the existence of a tension, let alone its magnitude, has ever been made."

Many investigators are seeking to discover the precise nature of the forces that cause adsorption. Rideal[3] distinguishes two main types of adsorption at solid surfaces, van der Waal's adsorption and chemi-adsorption, and divides the latter into two types, depending upon whether the adsorbed molecules are held by Coulomb forces or by co-valency forces. De Boer and Custers[4] attempt to evaluate the relative magnitudes of these different forces. In discussing the flotation of graphite by xanthate we have attributed[5] the adsorption of xanthate to specific interatomic forces of the crystal lattice, which necessarily become unsaturated at the surface. These forces may vaguely be described as "chemical" and to this extent our views coincide with those of Taggart and his collaborators. We consider, however, that their view is too restricted and that they are wrong alike in denying adsorption and in seeking to attribute the formation of all surface films to metathesis reactions that yield identifiable insoluble compounds.

Taggart, del Giudice and Ziehl themselves make use of the conception of adsorption, though they do not call it by its accustomed name. Thus, it is claimed that for the flotation of copper minerals and of sphalerite coated by copper sulfide it is first necessary for the surface to become oxidized to copper sulfate or some other soluble copper salt, and that, without leaving the region of the surface, this reacts with xanthate by double decomposition (metathesis) to give an adherent film of "copper xanthate." But copper sulfate is highly soluble; why does it not leave the surface as fast as it is formed? The authors state that copper sulfate cannot readily be removed from such surfaces by washing with water, but this does not explain the assumed phenomenon. In an endeavor to avoid using the conception of adsorption for the xanthate film, the writers have postulated a tenacious holding to the surface of soluble copper. This surely is a classic illustration of the phenomenon of adsorption.

It is necessary to examine some further examples of the application of their theory to see just what Taggart and his associates mean by "simple chemical reactions." Gold, it is claimed, cannot directly acquire a surface coating of xanthate ions. Only after the surface has been made more soluble than gold xanthate, by interaction with aqua regia or cyanide, can it react with xanthate. Here again the conception of adsorption is invoked in postulating that a film of soluble gold chloride or cyanide or the like is retained at the surface of the gold. The surface of galena likewise must first be converted to something more soluble than lead xanthate before it can adsorb xanthate; the lead sulfate assumed to be formed on the surface is stated to be less soluble than that of bulk lead sulfate and cannot be removed by washing with water. Once again the "chemical theory" is apparently based on a hypothetical adsorption. To explain the action of nitrogenous collectors, Taggart seeks by analogy to show that they can form insoluble compounds with the heavy metals.

The essential feature of Taggart's "chemical theory" is, then, that a collector film is always formed by interaction between a surface (or surface coating held to the surface by a not so simple chemical force) of moderate solubility, and another radicle, the result being to produce a less soluble identifiable surface film. Thus the theory is, in essence, a solubility theory. However, in stating that there is no limitation as to the nature of the chemical reaction postulated, the sponsors of the theory appear to doubt whether their present views, based as they are on solubilities, are sufficiently comprehensive. Much of our own early work was conducted with the hope of verifying Taggart's theory—so attractive because of its simplicity—and it was a disappointment to find, from time to time, experimental evidence that could not be reconciled with it. All that we can now retain of the theory is the generalization: "The capacity of a mineral to adsorb a soluble chemical collector containing sulfur is closely related to the solubility of the salt formed by the collector and the metal of the mineral," which we use as a guide to experimental work. But this is not a complete theory: it is insufficient, since orientated adsorption may occur when analogous insoluble salts are unknown.

Taggart, del Giudice and Ziehl may have confused double decomposition and exchange adsorption. The distinctive feature of both processes is that an ion from the lattice passes into solution for each ion that is adsorbed. Initially the two processes would lead to much the same surface conditions but they differ primarily in that exchange adsorptions occur at lower concentrations of the metal ion and of the collector than are required to form precipitates by double decomposition. Furthermore, exchange adsorption ceases with the formation of a unimolecular film, whereas double decomposition tends towards completion, although, of course, as in all reactions of this type involving solid phases, the reaction would soon become very slow because of the protective effect of surface coatings. It will be apparent that the mere proof that an ion from the solution replaces one from the surface and vice versa cannot differentiate between the two processes. Since lead sulfide is less soluble than lead ethyl xanthate, double decomposition between galena and potassium ethyl xanthate is inconceivable, but exchange adsorption is conceivable. Double decomposition and exchange adsorption are both conceivable between lead sulfate and potassium ethyl xanthate.

Taggart, del Giudice and Ziehl would have us believe that the lead ions forming part of the surface of a galena crystal behave in precisely the same manner as lead ions free-swimming in solution, and that they will not bind the ions of a soluble collector to the surface unless lead ions in the solution would give a precipitate with that collector[1]. The behavior of a naval rating on review is vastly different from his behavior on leave. Likewise a lead ion held in its allotted place in the crystal lattice, surrounded for the most part by sulfide and other lead ions, cannot be expected to have the same characteristics as a lead ion free-swimming in solution, surrounded by water molecules. We freely admit that there is a marked analogy between adsorptive power and insolubility; this has been pointed out by workers in other fields, particularly in connection with exchange adsorption. But again we stress that in flotation we find on closer investigation only an analogy, not an identity.

Our discussion on the adsorption of collectors involves three main issues: (1) the assumed identity of the adsorbed film of a soluble collector of the xanthate type with known salts; (2) the mechanism of the formation of the film, and (3) the nature of the adsorbed film when insoluble metallic salts of the collector are unknown. The adsorption of activators and of depressants—if these are adsorbed—should be considered as a separate problem, since it is well known from the studies of Langmuir, Adam, Rideal, Marcelin and others that solutions of polar nonpolar organic compounds, to which class all known collectors belong, have highly special surface properties.

## Is the Adsorbed Film Identical with Known Salts?

In a recent publication[5] we have shown on theoretical grounds why the force holding a unimolecular film of xanthate ions to the surface of a lead mineral must, of necessity, differ from the force holding the outermost layer of xanthate ions to the crystal lattice of lead xanthate in bulk. These theoretical considerations do not, however, lead to a quantitative measure of the differences in this or any other similar case. Experimental evidence is necessary then to decide how far the properties of the adsorbed film of any assumed "compound" differ from those of that compound in bulk.

The work of Paneth and Horowitz[6] on the adsorption of radioactive elements by barium sulfate and barium chromate showed that those elements are adsorbed best which form highly insoluble sulfates and chromates. On the other hand, radium, whose chloride and oxide are easily soluble, is not adsorbed by silver chloride or chromic oxide. Here again is a parallelism between adsorption and solubility, such as has been stressed by Taggart for the xanthates. But Freundlich states explicitly that the concentration of the radioactive element was so small in the solutions from which it was adsorbed that the solubility product of none of its salts could have been reached. Thus, for example, radium sulfate cannot exist as such, when radium is adsorbed by barium sulfate.

Similar evidence that the surface film is not identical with an insoluble salt is given by the work of Kolthoff and Rosenblum[7] on the adsorption of dyes by lead sulfate. They ascribe the adsorption to an ionic interchange at the surface between the sulfate ions and the dye ions, but say: "This reaction is limited only to the surface, the solid lead Ponceau salt is not in equilibrium with the system as its solubility product is not exceeded." Further similar evidence is given in a later paper[8] on the adsorption of wool violet by lead sulfate.

Gaudin and Hansen[9] indicate that the heptoate radicle is adsorbed by calcite before a precipitate of calcium heptoate can be formed in the solution from which the heptoate is being adsorbed. Here again the adsorbed film differs in its properties from calcium heptoate.

Held and Somochwalov[10] show that barium sulfate is capable of adsorbing laurate ions from a sodium laurate solution. They assume that there is an exchange between sulfate and laurate ions. Why there should be such an exchange puzzles them, for, from the solubility products of barium laurate and barium sulfate, one would not expect the reaction $BaSO_4 + 2Na\,Laurate = Ba(Laurate)_2 + Na_2SO_4$ to occur. The solubilities of barium laurate and of barium sulfate are reported to be 0.008 grams and 0.00023 grams respectively in 100 grams of solution.

In much of our work on the action of cyanide in preventing contact at mineral surfaces, it was found that adsorption occurred from solutions in which no metallic xanthates had been precipitated, though there was a comparatively high concentration of metal and xanthate present in solution. Metal-cyanide complex formation prevented the solubility product of the metal xanthate being exceeded, consequently solid metal xanthate could not have been present in those tests and could not have constituted the surface film.

Taggart[11] has expressed the opinion that the solubility of what he and his collaborators regard as a surface film of metal salt is less than that of the same salt in bulk.

## Mechanism of Formation of Film

The argument of Taggart, del Giudice and Ziehl[1] that adsorption—as distinct from double decomposition—could not change the xanthate ion sufficiently for it to become air-avid, is easily met. Professor Taggart more than anyone else has contributed to our knowledge that collector molecules and ions belong to the polar nonpolar type, possessing one end that is water-avid and one end that has some air avidity. If, as the "adsorptionists" claim, the polar end is binding the collector to the mineral, the nonpolar end is orientated outwards, and the surface will certainly *not* "retain its water-avid character after adsorption." If there is any difficulty on this score, it is more troublesome to the Taggart theory. It is easy to understand why a film of collector, adsorbed directly on to the crystal lattice, should be orientated. It is not so easy to understand why a compound formed by double decomposition between the collector and a loosely held layer of soluble sulfate should be deposited on the surface in any ordered manner.

Sodium sulfide is added in practice to help in the flotation of lead sulfate. The sulfide converts a thin film of the sulfate to sulfide; Taggart, del Giudice and Ziehl suggest that this film is then partly oxidized back to sulfate. This outermost film reacts with ethyl xanthate by double decomposition, but, being thin, does not consume an excessive amount. In the final state the xanthate film must evidently be directly above the lead sulfide, all the outermost sulfate having been removed. It will be apparent that if one can float anglesite or cerussite in the presence of sodium sulfide, this theory is inadequate. We have shown[12] that contact can be established between an air bubble and anglesite in the presence of potassium amyl xanthate in spite of the addition of as much as 150 mg. per liter of $Na_2S.9H_2O$. This applies over a wide range of pH values. Cerussite can tolerate an addition of 60 mg. per liter of the sulfide under similar conditions.* Both anglesite and cerussite can tolerate an addition of sodium sulfide of at least 25 mg. per liter without losing their response to 25 mg. per liter potassium ethyl xanthate, and it has been shown that a considerable fraction of the added sulfide remains unchanged.

Despite the vast amount of work that has had as its objective the explanation of the flotation of galena by ethyl xanthate, the problem is not yet solved. There are several aspects of this problem on which we wish to comment, since they have a bearing on the contention that filming by sulfate is essential before any reaction with xanthate can occur.

Firstly, we have shown[13] that, using sodium aerofloat as collector, galena can be activated by copper sulfate, and that in 25 mg. per liter KEtX solution, galena (above its critical pH value, 10.4) can also be activated by copper sulfate; the activation is similar to that of sphalerite. Almost all writers agree that the latter activation may be represented by the action $ZnS + Cu^{++} \rightarrow Zn^{++} + CuS$. By analogy the activation of galena should be represented thus: $PbS + Cu^{++} \rightarrow Pb^{++} + CuS$. Taggart, however, considers that the surface consists very largely of lead sulfate, but from solubility considerations the reaction $PbSO_4 + Cu^{++} \rightarrow Pb^{++} + CuSO_4$ is impossible. Consequently Taggart must assume that, when galena is activated by copper salts, sulfate for the time being is conveniently absent from the galena surface, or at least nearly so.

---

* This difference between anglesite and cerussite is difficult to account for by any theory of the action of flotation reagents. Activation by copper sulfate seems to give an almost identical surface, no matter whether the mineral activated is stibnite, sphalerite or galena. Why should not activation by sodium sulfide follow a similar course?

Secondly, we have been able to show that galena may be floated in the presence of a limited amount of sodium sulfide, the actual concentration being dependent upon the collector used. Fig. 1 shows for parallel contact tests the amount of sulfide that can be tolerated without preventing contact when using two different concentrations of sodium di-ethyl dithiocarbamate as collector, plotted in relation to the pH value. Some sulfide remained in solution throughout these tests: its presence could be detected by its odor and by the color of the precipitate given by lead nitrate. In similar work with ethyl xanthate it has been shown (q.v.) that very little sulfide is lost or consumed during the tests. Admittedly the concentration of sulfide that can be tolerated is not very great, but it increases with the concentration of the collector. Now, according to the Taggart theory, provided there is *any* sulfide present, sulfate formation should be prevented, and contact should be impossible whatever the collector concentration. Direct adsorption of collectors of the xanthate type by lead sulfide must be responsible for the excellent flotation of galena that we have found in the presence of more than one gram per liter sodium sulfide when using 200 mg. per liter potassium di-n-amyl dithiocarbamate as collector; contact tests confirm this, since at pH values below

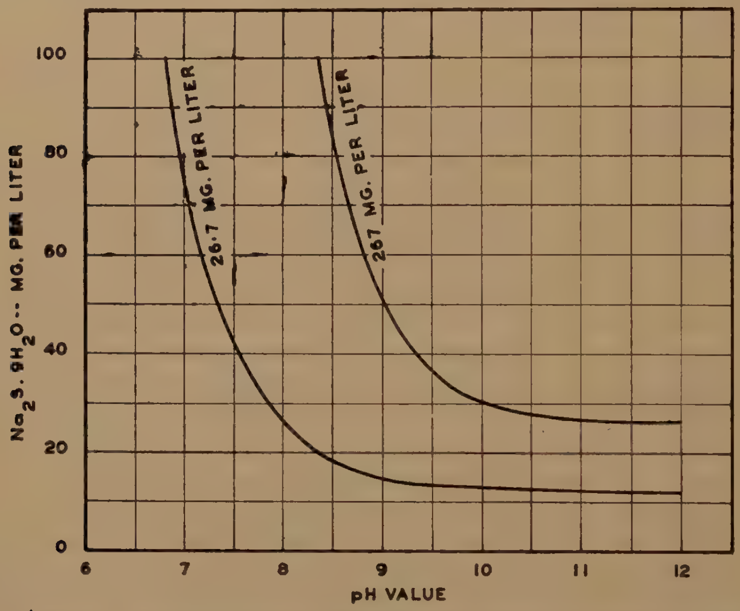


FIG. 1.—AMOUNT OF SULFIDE THAT CAN BE TOLERATED WITHOUT PREVENTING CONTACT

12, an amount of 50 mg. per liter of the collector induces contact in a 1 gram per liter sulfide solution. Flotation is possible under similar conditions in an atmosphere of nitrogen, iso-amyl alcohol being a suitable frother. The corresponding n-butyl compound has a similar effect.

These results for the two higher dithiocarbamates do not provide absolute disproof of the Taggart theory. It is possible that the lead salt of di-n-butyl dithiocarbamate is less soluble than lead sulfide and that the adsorption of the dithiocarbamate could then be described as a double decomposition between lead sulfide surface and collector. But a similar explanation is not applicable to the results for the di-ethyl dithiocarbamate, since its lead salt is definitely more soluble than lead sulfide. This was proved by adding sufficient lead nitrate to precipitate slightly more than half the acid radicles from an equimolecular mixture of sodium sulfide and sodium di-ethyl dithiocarbamate in solution. The precipitate, which was almost black, was coagulated and filtered; a second addition of lead nitrate to the filtrate gave a grayish yellow precipitate that seemed to be almost pure lead di-ethyl dithiocarbamate.

This work with sodium sulfide suggests a competitive adsorption at the mineral surface between hydrosulfide and collector ions, and this adsorption may also exist even when no soluble sulfide has been added. There would be either a direct adsorption of one or both ions by lead sulfide or an "exchange adsorption" in which the sulfide ions of the crystal lattice take part in the equilibrium. If sulfide ion is liberated when xanthate is adsorbed by pure sulfide minerals the adsorption must be of the latter type. Experimental verification of either hypothesis has been prevented by difficulties in obtaining ground and sized galena (or other sulfide minerals) free from oxidized compounds and in detecting or estimating the very small quantities of reagents involved. A. F. Knoll concluded[14] from an investigation of the reactions of oxidized galena with ethyl xanthate that the xanthate ions abstracted by galena were replaced by an equivalent concentration of carbonate, sulfate and other sulfoxide ions, and that there was no displacement of sulfide by xanthate. An examination of his methods and results has failed to satisfy us that these claims are fully substantiated.

With the quantities of galena and xanthate solutions used by Knoll, and assuming cubic particles of average size 400 mesh (stated to be −200 mesh) the amount of potassium ethyl xanthate required for the formation of a complete unimolecular film would be only about 2 mg. per liter. This would liberate 0.2 mg. per liter $S^{--}$, which is only three times the minimum concentration that can be detected by the method used by Knoll under the most favorable conditions. But the test is done in strongly acid solutions and we find that sulfoxides derived from partly oxidized galena can destroy considerably more than this quantity of sulfide. Furthermore, it must be remembered that the relationship between sulfide concentration, pH value and adsorption of xanthate recently given by us (ref. 12, Fig. 5) further limits the maximum concentration of sulfide to be expected, irrespective of particle size. Knoll's failure to detect sulfide ion cannot therefore be regarded as proof that it is not liberated. The concentrations of xanthate abstracted and of sulfate liberated by the oxidized galena, as measured by Knoll, varied from approximately 5 to 40 times the amounts that are required for a unimolecular surface reaction; furthermore, sufficient accuracy was not attained in the analyses for total anions for conclusions to be drawn concerning the final unimolecular layer of xanthate, the formation of which, as already stated, requires only 2 mg. per liter of xanthate. Knoll's investigation concerned, indeed, not the primary flotation reaction, but simply the action of ethyl xanthate on bulk lead sulfate and similar compounds.

Following Knoll's technique to some extent, we also attempted to determine whether sulfide is liberated from sulfide minerals by collectors. The methylene blue test for sulfide, as recommended by Knoll[15], was used and, employing galena and chalcopyrite from large apparently unoxidized massive specimens, the blue color that is supposed to be characteristic of sulfide ion was obtained. Subsequent tests showed, however, that even in the presence of xanthate the same galena and chalcopyrite completely abstracted the sulfide from solutions containing as much as 30 times the amount of sulfide that had apparently been previously liberated by the xanthate. This test for sulfide is useless, therefore, in this connection. Much more detailed and accurate work, carried out in the absence of oxygen, is necessary before work of this type can give reliable conclusions.

In attempting to explain the depressant action of chromates, Taggart, del Giudice and Ziehl state that lead chromate is less soluble than lead ethyl xanthate and that therefore chromate ion at the surface of a lead mineral cannot be displaced by the xanthate ion from solution. However, Knoll[14], who worked in Taggart's laboratory, claimed that ethyl xanthate is abstracted from solution by lead chromate, an equivalent amount of chromate ion passing into solution. This seems to be a typical example of exchange adsorption. We have found that crocoite, the naturally occurring lead chromate, can be floated by high concentrations of ethyl xanthate. Suspecting that the mineral, though it appeared to be pure, might have contained some more soluble impurity, we made a synthetic fused lead chromate for comparison with it. The floatability of this synthetic lead chromate proved to be practically identical with that of natural crocoite. The frother used—50 mg. per liter terpineol—produced practically no flotation. Ethyl xanthate added in gradually increasing amounts first caused appreciable flotation at about 200 mg. per liter. With double this concentration, good flotation was obtained. Contact tests, supplementing those reported previously[16], showed, however, that contact is hindered by the formation of a precipitate on the surface. With concentrations of 500 mg. per liter KEtX and over contact was readily established, and immediately after the surface was freed from the precipitate by wiping, angles of contact between 53° and 58° were obtained.

Marcasite and pyrite, though of identical chemical composition, $FeS_2$, are by no means identical in their flotative properties. Fig. 2 shows, for the two minerals, the relationship between the pH value and the concentration of sodium cyanide necessary to prevent contact between an air bubble and the surfaces of the minerals immersed in a 25 mg. per liter KEtX solution. According to the Taggart hypothesis, the difference in the response of the two minerals must be attributed to oxidized surface films of different chemical composition. But because of the chemical identity of the minerals, any oxidation products must be identical. On the other hand, the difference in the crystal structure of the two minerals must give rise to different surface forces, consequently it would be anticipated that the adsorption of xanthate on a marcasite surface would differ quantitatively from the adsorption of xanthate on pyrite.

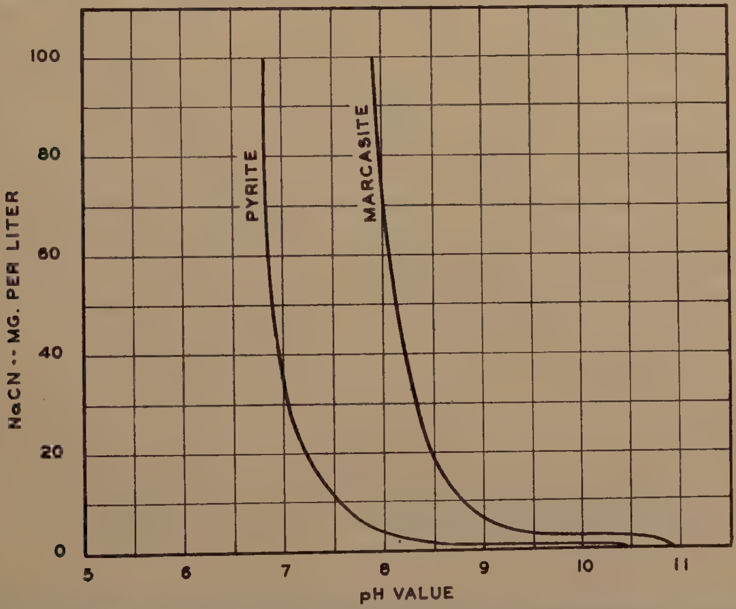


FIG. 2.—RELATIONSHIP BETWEEN pH VALUE AND CONCENTRATION OF SODIUM CYANIDE NECESSARY TO PREVENT CONTACT BETWEEN AIR BUBBLE AND SURFACES OF MINERALS IMMERSED IN 25 MG. PER LITER KEtX SOLUTION.

Taggart and his associates claim that pure gold is unaffected by a solution of potassium ethyl xanthate, and that it responds only after pretreatment with a solution in which it is slowly dissolved. With the purest gold obtainable in Melbourne we obtained contact without such pretreatment. The gold used in our tests was a substandard specimen from the Royal Mint, at least 99.99 per cent pure. We have communicated with Professor Taggart, telling him of our results, in the hope that between us we may find the reason for the discrepancy.

## Do All Salts Postulated by Taggart Hypothesis Exist?

The Taggart hypothesis would not have been formulated had the heavy metals not formed relatively insoluble salts with collectors of the xanthate type. It is pertinent to inquire, however, whether salts are known corresponding to the flotation of every mineral by compounds that have been proved to be collectors for it. Here one encounters three types of apparent exceptions that seem to us to be fatal to the general validity of the theory.

Graphite and sulfur adsorb the xanthates and their flotation is thereby improved. These facts cannot be reconciled with Taggart's theory. Neither carbon nor sulfur forms a known xanthate, and it is unlikely that such compounds will be shown to have a separate existence.

Many of the simple amines are collectors for the sulfide minerals[17]. Other types of nitrogen-bearing compounds are also collectors. In attempting to apply their theory to these nitrogenous collectors, Taggart, del Giudice and Ziehl cite, as "persuasive evidence," a number of insoluble compounds formed between heavy metals and nitrogen-bearing organic compounds. One can well believe that these examples were chosen, as they state, more or less at random. Thus, what they style "compounds" between p-nitrobenzene azo-resorcinol and magnesium, nickel and cobalt are in reality lakes[18]. The magnesium lake is described[19] as magnesium hydroxide upon which the dyestuff is *adsorbed.* In the formation of the compound between aluminum and $\alpha$-hydroxy-quinoline, to which the authors also refer, the aluminum reacts with the hydroxyl group, not with the nitrogen atom; consequently $\alpha$-hydroxy-quinolin is not a happy choice in discussing nitrogenous collectors. p-dimethyl-amino-benzal rhodanine should not have been cited to support claims concerning the nitrogenous collectors since, being a derivative of a di-thio acid, its reactivity would be better attributed to its sulfur-bearing group. Cadmium forms a precipitate, not with ethylene diamine as stated but with a mixture of potassium iodide and copper ethylene-diamine nitrate. The composition of the precipitate is $(Cu(en)_2)(CdI_4)$[20]. It is the copper, not the cadmium, that is bound to the diamine, forming an ion similar to the cuprammonium ion $Cu(NH_3)_4^{++}$. The evidence for benzidine is inconclusive, for Knorra describes[21] the compound with tungsten as a tungstate and indicates that the reaction with iron is a reduction. The corresponding copper compound is a complex cupramine iodide[22] $(Cu\ Benz)I_2$. Most of the other compounds mentioned by Taggart and his associates are oximes, thus containing an acidic *hydroxyl* group with which the metals react.

The fact that not a single mon-amine has been cited as forming a precipitate with a heavy metal salt is surely evidence that the theory is inapplicable to the amines. Though such precipitates have been sought in this laboratory, none has been found. However, from contact-angle measurements we have already concluded that the adsorption of the amines differs in type from the adsorption of xanthates. Hence, although no valid evidence has yet been adduced by its sponsors in support of the chemical theory for the amines, we do not claim that this proves that the theory is inapplicable for the xanthates.

There is quantitative evidence that adsorption does occur in many cases where the analogous salts are not insoluble. Almost every textbook of analytical chemistry stresses the important effect of adsorption of soluble salts by insoluble precipitates: see, for example, Hall[23]. Barium sulfate adsorbs many soluble salts, such as barium nitrate, barium chlorate, ferric chloride and chromium chloride. G. A. Ampt, of this department, has determined, for barium sulfate and a number of soluble salts, the relationship between adsorption and the concentration of the adsorbed salt. Figures obtained for the determination of sulfate in the presence of potassium nitrate are tabulated below; barium chloride was used to precipitate the sulfate from standard sulfuric acid solution.

| WEIGHT OF BARIUM SULFATE PRECIPITATE | CONCENTRATION OF $KNO_3$ DURING PRECIPITATION |
|---|---|
| 0.2403 | 0 |
| 0.2450 | 0.1-N |
| 0.2484 | 1.0-N |

The amount of barium nitrate adsorbed from a solution normal with respect to the nitrate radicle was 3.5 per cent of the weight of the barium sulfate. Hall states that "the surfaces of all solids exert an attractive force upon substances in solution" and: "Such an attractive force results from the fact that the forces of the component parts of a solid are not so fully satisfied at the surface as in the interior." This is not a complete explanation of such adsorptions, but it is manifestly impossible to apply the Taggart hypothesis in these cases. The basis of analytical chemistry may not be quicksand, but even on this well-known ground one needs to walk warily.

## ACTIVATORS

There seems to be general agreement concerning the mechanism of the most common examples of activation. For sphalerite and copper sulfate the action generally agreed to be responsible for the activation is $ZnS + Cu^{++} \rightarrow CuS + Zn^{++}$. From considerations of the solubilities of the sulfides concerned, the reaction should proceed almost to completion in the direction shown, if given sufficient time. Hence there is no need to look for any other explanation, although the reaction could be regarded as an exchange adsorption. Still, as Taggart and his associates point out, further quantitative work on activation is necessary to establish a general theory that solubility alone is the controlling influence.

In the dilute solutions used in flotation, however, it is probable that the reaction does not proceed much beyond the unimolecular film stage[24]. Consequently, activated sphalerite would not be expected to have the same adsorptive properties as massive copper sulfide. Taggart, del Giudice and Ziehl, however, regard the fact that in certain adsorptive properties the activated sphalerite more closely resembles chalcopyrite than covellite, as being in some way opposed to an adsorption. It seems to us that the differences between the reactions of each of the minerals chalcocite, covellite, bornite, chalcopyrite and activated sphalerite, with alkali, cyanide and xanthate, prove that the reacting surface in each case is not, as they suggest, simply a film of copper sulfate, but is the mineral itself.

## DEPRESSANTS

There is very little quantitative evidence concerning the actions of the common depressants. It is generally accepted that the action of cyanide in preventing the flotation of sphalerite is to convert the copper in solution or already on the sphalerite surface to a soluble cupricyanide complex, thus reducing the copper ion concentration to less than that at which it can activate sphalerite. With other minerals there is no conclusive evidence as to whether cyanide forms surface films. From our own work, Taggart, del Giudice and Ziehl suggest that an iron-copper-cyanide complex is the important factor in determining the effect of cyanide on iron and copper minerals, and they also suggest that there are formed insoluble surface coatings perhaps of cupricyanide or ferricyanide. Such evidence as there is points equally well to a competitive adsorption by the mineral surface between the depressant (cyanide or complex cyanide ions) and the collector, the competition being influenced by their relative concentrations. A third possibility is that the cyanide functions indirectly by reducing the metal ion concentration to a value so low that the "adsorption solubility product" is not reached. The choice between these theories ultimately depends therefore on accurate determinations of the solubilities and degrees of ionization of all the possible reactants. Whichever theory survives, the controversy will have served the highly useful purpose of opening up fields of research that must lead to a better understanding of the action of flotation reagents. In the development of the subject both the adsorption theory and the chemical theory have played useful parts.

## ACKNOWLEDGMENTS

This work has been carried out for the following companies: Broken Hill South Ltd., North Broken Hill Ltd., Zinc Corporation Ltd., Electro-

lytic Zinc Co. of Australasia Ltd., Mt. Lyell Mining & Railway Co. Ltd., and the Burma Corporation Ltd. The authors desire to express their thanks to Mr. H. Hey, under whose general direction the work has been carried out, and to Prof. E. J. Hartung for having provided accommodation in the Chemistry Department of the University of Melbourne.

## REFERENCES

1. A. F. Taggart, G. R. M. del Giudice and O. A. Ziehl: *Trans.* A.I.M.E. (1934) **112,** 359, 364, 385.
2. Adam: The Physics and Chemistry of Surfaces. Oxford, 1930. Clarendon Press.
3. Rideal: *Nature,* Jubilee Number (1935).
4. De Boer and Custers: *Ztsch. phys. Chem.* (1934) **25,** 225.
5. Wark and Cox: *Jnl. Phys. Chem.* (1935) **39,** 797.
6. Freundlich: Colloid and Capillary Chemistry, 220. London, 1926.
7. Kolthoff and Rosenblum: *Jnl.* Amer. Chem. Soc. (1933) **55,** 2664.
8. Kholthoff, von Fischer and Rosenblum: *Jnl.* Amer. Chem. Soc. (1934) **56,** 832
9. Gaudin and Hansen: Flotation Fundamentals, I. Univ. of Utah, 1928.
10. Held and Somochwalov: *Koll. Ztsch.* (1935) **72,** 13.
11. Taggart: *Trans.* A.I.M.E. (1930) **87,** Milling, 247.
12. Wark and Cox: Page 7, this volume.
13. Wark and Cox: *Trans.* A.I.M.E. (1934) **112,** 267.
14. Knoll: Dissertation, Columbia University, 1932. Partly printed in *Trans.* A.I.M.E. (1934) **112,** 382.
15. J. H. Yoe: Photometric Chemical Analysis, **1,** 373. New York, 1928. John Wiley & Sons.
16. Wark and Cox: *Trans.* A.I.M.E. (1934) **112,** 189.
17. Wark and Wark: *Jnl. Phys. Chem.* (1935) **39,** 1021.
18. Ruigh: *Jnl.* Amer. Chem. Soc. (1929) **51,** 1456.
19. British Drug Houses, Reagents for Spot Tests. London, 1934.
20. Spacu and Sucin: *Ztsch. anal. Chem.*, **77,** 34.
21. Knorra: *Ber.* (1905) **38,** 783.
22. Spacu: *Ztsch. anal. Chem.* **67,** 31.
23. Hall: Textbook of Quantitative Analysis, 141. New York, 1930.
24. Ravitz and Wall: *Jnl. Phys. Chem.* (1934) **38,** 13.

## DISCUSSION

*(Arthur F. Taggart presiding)*

R. S. DEAN,* Washington, D. C.—The selection of pyrite and marcasite as examples of minerals that, having the same composition, would form the same oxidation product was a particularly unhappy one. The recognized method for distinguishing pyrite and marcasite when they occur massively so that the crystal form cannot be ascertained is oxidation with a solution of ferric sulphate, a procedure first developed by Stokes and later modified by Allen. The proportion of sulphur and sulphuric acid obtained by this oxidation is very different for the two minerals.

A. F. TAGGART,† New York, N. Y.—The authors' assertions with respect to activation of sulphur and graphite by xanthates and abstraction of xanthates from solution by these substances, were, of course, definitely worrisome from the point of view of the chemical theory. The results of our work in checking their results are to be found in the paper beginning on page 180 of this volume. We are, of course, open to conviction that there are flotations with soluble reagents that do not involve chemical reaction between the collector and the substance floated, but our invariable experience has been that when we try to float materials under conditions where we were assured of reasonable purity and the absence of oily substances, we do not get flotation when chemical reaction is not a possibility.

---

* Chief Engineer, Metallurgical Division, U. S. Bureau of Mines.

† Professor of Ore Dressing, Columbia University.

Now so far as difference between exchange adsorption and chemical reaction is concerned, to us that has seemed a matter of difference in terminology rather than difference in facts. We certainly would not quarrel with any man that wanted to use a different terminology.

B. M. Bird,* Columbus, Ohio.—It seems to me that I remember seeing some work on very pure minerals where great care was taken and the experimenters were unable to float them. If correct, this fact would have an interesting bearing on the adsorption versus the chemical-reaction theories of flotation. I wonder why the point has not come up before.

A. F. Taggart.—We have done some work on silica. When you attempt to float nonmetallic mineral away from silica with oleates, under certain circumstances the silica tends to come up with the other nonmetallic mineral. One of the activators of silica is iron in solution. In a flotation operation that means ferric iron, unless some considerable excess of reducing agent is added to the pulp. We found in some experiments in which we agitated granular silica with iron fillings for different lengths of time that with something like 5 min. shaking in a test tube or stirring in an open beaker, the pulp became distinctly discolored and within about 15 min., it was almost a chocolate brown. If we separated the silica from pulps that had been thus treated for various times, whenever the dry silica in a test tube, compared side by side with some untreated silica, showed a visible difference in color, it would float with oleate, but if there was no visible difference, it would not float.

We found also, by examining the polished surfaces of silica that had been treated with iron, that there were small visible yellowish brown patches on the surface of the silica that were of the same color as ferric silicate, formed by precipitation from a water glass solution. We found that whenever the polished surface was thus discolored, there was activation in sodium oleate solution.

---

* Chief Concentration Engineer, Battelle Memorial Institute.

# Principles of Flotation, VI—Influence of Temperature on Effect of Copper Sulphate, Alkalies and Sodium Cyanide on Adsorption of Xanthates at Mineral Surfaces

By Ian William Wark* and Alwyn Birchmore Cox*

(New York Meeting, February, 1938)

Different parts of the world in which mineral separation by flotation is practiced experience vastly different natural temperatures, and in some districts there is a big difference between summer and winter temperatures. It will be shown in this paper that the temperature is of considerable importance where it is desired to separate pyrite or arsenopyrite from other minerals. It is probable that some of the differences obtained in the flotation of these minerals at plants working under otherwise similar conditions are due to temperature variations. The influence of temperature on the flotation of galena, chalcopyrite and sphalerite by xanthates is less marked than its influence on pyrite flotation.

## Experimental Method

The methods used have been described previously.[1-4] In each test the clean mineral specimen was immersed in a solution prepared by adding the reagents in the following order: (1) sodium carbonate and hydrochloric acid as necessary to buffer the solution and to give approximately the pH value desired, (2) sodium cyanide, (3) copper sulphate, (4) ethyl xanthate, followed by (5) a final adjustment of pH value. After ½ hr. the mineral was tested for a xanthate film by bringing a bubble of air into apparent contact with the submerged polished surface. If true contact (spreading) was not obtained within ½ min. and after cleaning the surface by wiping with a small linen pad, it was concluded that the adsorption of a xanthate film had been prevented. Following the method already described (ref. 2), curves have been constructed such that for a solution composition corresponding to any point below the curve, contact between mineral and air is possible, whereas for a solution composition corresponding to any point above the curve, contact is impossible.

---

Manuscript received at the office of the Institute Aug. 16, 1937. Issued as T. P. 876 in Mining Technology, January, 1938.

* Department of Chemistry, University of Melbourne, Melbourne, Australia.

[1] Wark and Cox: *Trans.* A.I.M.E. (1934) **112,** 189.

[2] Wark and Cox: *Trans.* A.I.M.E. (1934) **112,** 245.

[3] Wark and Cox: *Trans.* A.I.M.E. (1934) **112,** 267.

[4] Wark and Cox: *Eng. and Min. Jnl.* (1936) **137,** 641.

The temperature was controlled to within 1° C. of the specified value, not only during the period of immersion of the specimen in the solution, but also while the solution was being prepared and while the surface of the mineral was being tested.

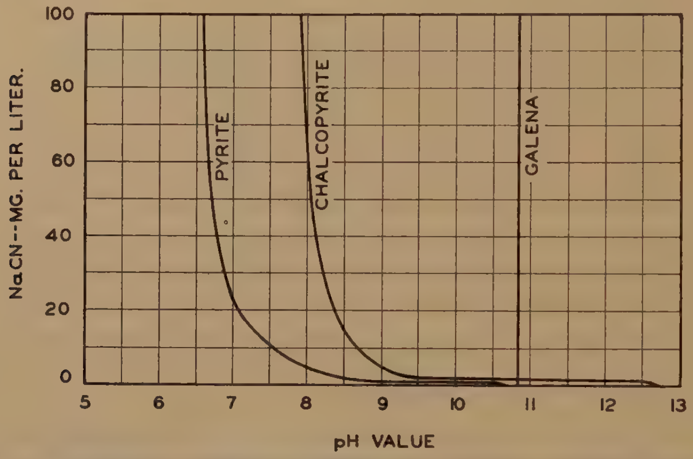


FIG. 1.—RELATIONSHIP BETWEEN CONCENTRATION OF SODIUM CYANIDE AND pH VALUE NECESSARY TO PREVENT CONTACT AT MINERAL SURFACES.
$CuSO_4$, nil. KEtX = 25 mg. per liter. Temperature, 10° C.

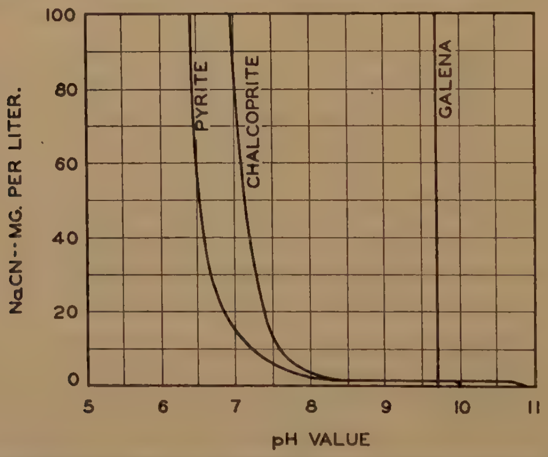


FIG. 2.—RELATIONSHIP BETWEEN CONCENTRATION OF SODIUM CYANIDE AND pH VALUE NECESSARY TO PREVENT CONTACT AT MINERAL SURFACES.
$CuSO_4$, nil. KEtX = 25 mg. per liter. Temperature, 35° C.

## EXPERIMENTAL RESULTS

*Ethyl Xanthate as Collector—No Added Copper Sulphate.*—Fig. 1 shows for 10° C. the relationship between the pH value and the concentration of cyanide necessary to prevent contact between an air bubble and surfaces of chalcopyrite, pyrite and galena respectively. Fig. 2 shows the corresponding relationships for 35° C. As there is no activator present, sphalerite does not respond to xanthate at any point within the diagram.

*Ethyl Xanthate as Collector—Copper Sulphate Present.*—Figs. 3 and 4 show, likewise, the relationship between the pH value and the concentration of cyanide necessary to prevent contact at 10° and 35° C., respectively, for pyrite, chalcopyrite and sphalerite in the presence of 150 mg. $CuSO_4.5H_2O$ per liter and with the standard concentration (25 mg. per liter) of ethyl xanthate. Fig. 5 shows the effect on the curves for pyrite and sphalerite of lowering the xanthate concentration to 5 mg. per liter, the temperature being 35° C.

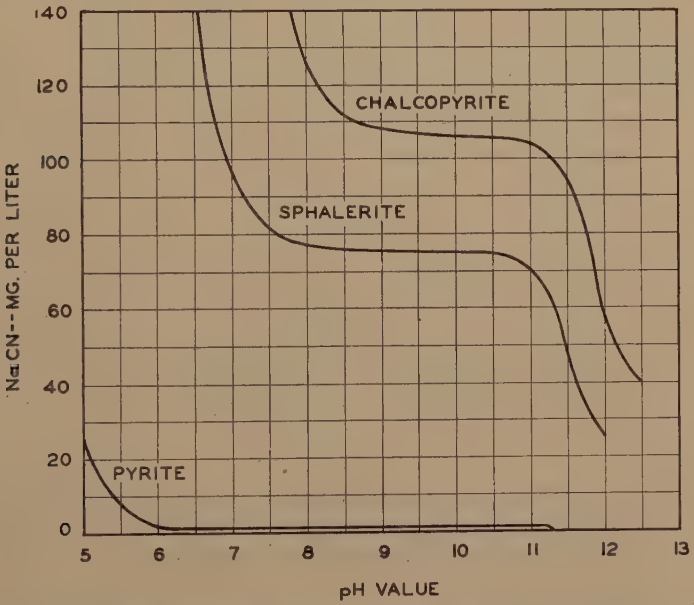


FIG. 3.*—RELATIONSHIP BETWEEN CONCENTRATION OF SODIUM CYANIDE AND pH VALUE NECESSARY TO PREVENT CONTACT AT MINERAL SURFACES.
$CuSO_4.5H_2O$ = 150 mg. per liter.
KEtX = 25 mg. per liter.
Temperature, 10° C.

At pH = 9.0, 70 mg. per liter of cyanide is necessary under these conditions to prevent contact at 35° C. at a sphalerite surface. It has been found previously (ref. 3, p. 276, curve 2, Fig. 6) that at room temperature a lower concentration (30 mg. per liter) suffices. For higher xanthate concentrations the effect of raising the temperature to 35° has been found to be negligible.

Fig. 6 shows, for a single pH value, namely 9.0, the relationship between the temperature and the concentration of cyanide necessary to

---

* See discussion on page 52.

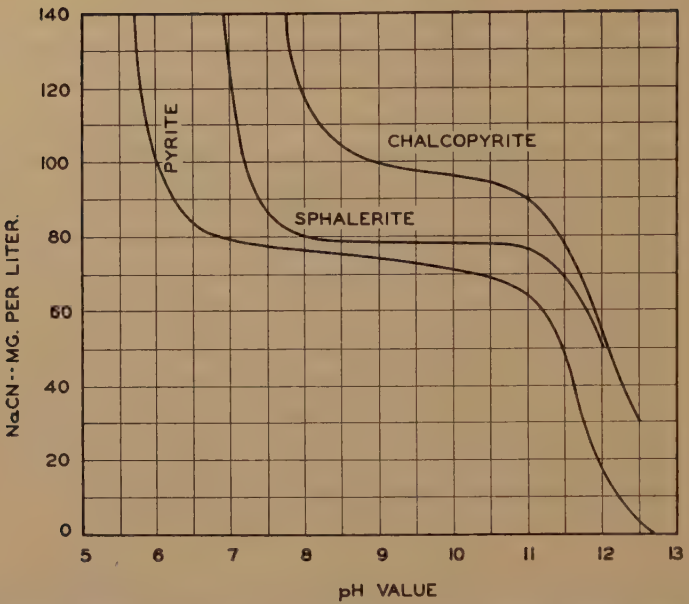


FIG. 4. RELATIONSHIP BETWEEN CONCENTRATION OF SODIUM CYANIDE AND pH VALUE NECESSARY TO PREVENT CONTACT AT MINERAL SURFACES.

$CuSO_4.5H_2O$ = 150 mg. per liter.
KEtX = 25 mg. per liter.
Temperature, 35° C.

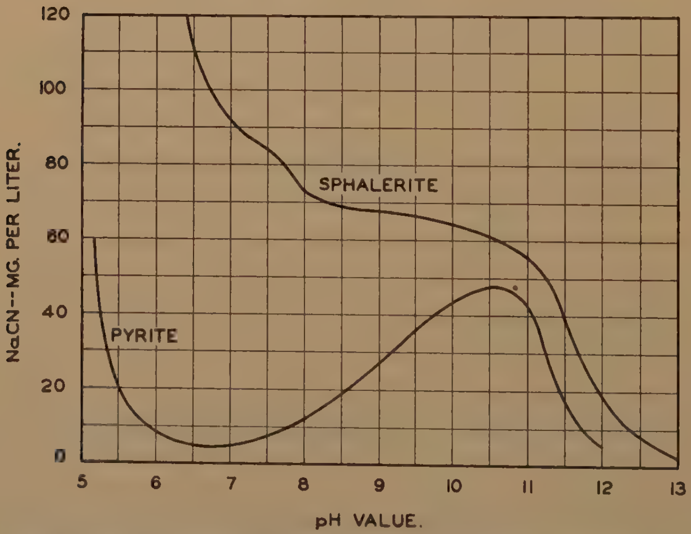


FIG. 5.—RELATIONSHIP BETWEEN CONCENTRATION OF SODIUM CYANIDE AND pH VALUE NECESSARY TO PREVENT CONTACT AT SURFACES OF SPHALERITE AND PYRITE.

$CuSO_4.5H_2O$ = 150 mg. per liter.
KEtX = 5 mg. per liter.
Temperature, 35° C.

prevent contact at the surface of pyrite. From the shape of the curves for pyrite in Figs. 3 and 4, it is apparent that the curve of Fig. 6 would need only slight modification for any pH value between 7 and 11.

The results of direct flotation tests with pyrite, carried out in stoppered cylinders, support the conclusions of the contact tests. The solutions used contained 25 mg. per liter potassium ethyl xanthate as collector, 20 mg. per liter terpineol as frother and 150 mg. per liter of $CuSO_4.5H_2O$. With 60 mg. per liter NaCN and at a pH value of 8.2, no flotation could be induced at 10° C., but at 35° C. flotation was excellent after a short conditioning period. With a more alkaline solution (pH = 10.0) and 5 mg. per liter of NaCN the results were similar. At 10° C. no flotation was possible even after a conditioning period of a day: the solution frothed well, however. When the solution was warmed to 20° C., fair flotation was obtained within half an hour. When the solution was again cooled, flotation of the pyrite ceased and when heated to 35° C. flotation was restored. Subsidiary tests showed that low temperature cannot by itself prevent contact: alkali and cyanide are also necessary.

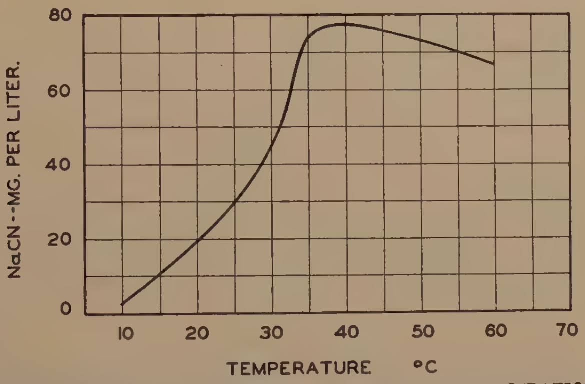


FIG. 6.—RELATIONSHIP BETWEEN TEMPERATURE AND CONCENTRATION OF SODIUM CYANIDE NECESSARY TO PREVENT CONTACT AT A PYRITE SURFACE.
$CuSO_4.5H_2O$ = 150 mg. per liter.
KEtX = 25 mg. per liter.
pH value, 9.0

*Amyl Xanthate as Collector—Copper Sulphate Present.*—Fig. 7, which should be compared with Fig. 4, shows, for pyrite and sphalerite, the effect of substituting for 25 mg. per liter of ethyl xanthate an equivalent quantity of amyl xanthate, the temperature being 35° C. The corresponding curve for sphalerite at 10° C. was also determined: it proved to be practically identical with the curve for sphalerite (not preactivated) previously determined at room temperature (ref. 3, p. 282) and thus lies somewhat lower than the curve of Fig. 7.

*Contact Tests on Arsenopyrite.*—The decision to investigate the effect of temperature in relation to air-mineral contact arose from an attempt to determine, at room temperature, the usual cyanide pH value curves for arsenopyrite. It happened that the temperature fluctuated severely from day to day and results could not be duplicated. As soon as the temperature was controlled, however, results became reproducible. The results for 35° C. determined as described above, indicated that the curve for arsenopyrite is almost identical with that given in Fig. 4 for pyrite. At pH values below 10 the curves for the two minerals are identical; at pH values above 10, arsenopyrite is a little more sensitive to depression, but the difference is very small. The arsenopyrite curve for 10° C. was not determined accurately, but we have found that it differs little, if at all, from that given in Fig. 3 for pyrite.

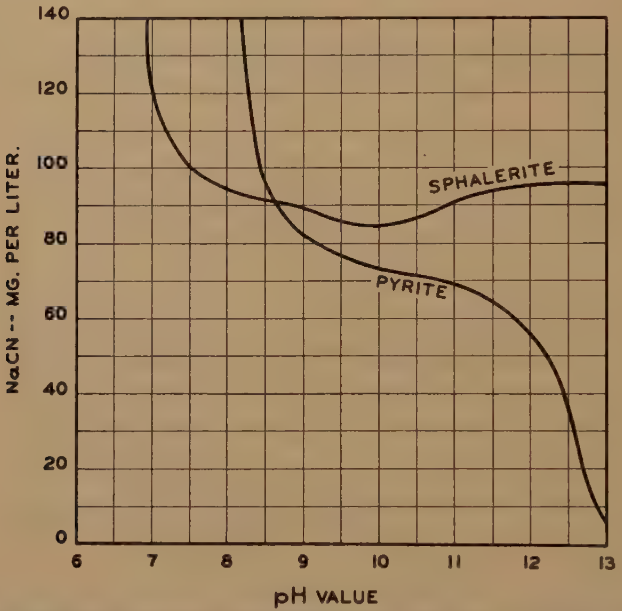


FIG. 7.—RELATIONSHIP BETWEEN CONCENTRATION OF SODIUM CYANIDE AND pH VALUE NECESSARY TO PREVENT CONTACT AT MINERAL SURFACES.

$CuSO_4.5H_2O$ = 150 mg. per liter.
KAmX = 31.6 mg. per liter.
Temperature, 35° C.

In the absence of copper sulphate, contact between an air bubble and an arsenopyrite surface seems to be wholly unaffected by cyanide. In a 25 mg. per liter xanthate solution the critical pH value, 7.0, was unchanged by cyanide additions. Galena is the only other mineral with which we have experimented that behaves similarly in this respect. This critical pH value was determined at room temperature before the need for accurate temperature control was realized; in the absence of copper sulphate, however, there is less need for temperature control (see Figs. 1 and 2).

## Discussion of Results

In the absence of copper sulphate, adsorption of xanthate is more easily prevented by alkali or by cyanide at 35° C. than at 10° C. There is, in fact, for each of the three minerals of Figs. 1 and 2, an increase in the critical pH value as the temperature is lowered, and there is likewise an increase in the critical cyanide-ion concentration.

Table 1.—*Variation in Critical pH Value and in Critical Cyanide-ion Concentration with Temperature*

KEtX = 25 Mg. per Liter

| Mineral | Critical pH Value | | Critical $CN^-$ Concentration | |
|---|---|---|---|---|
| | At 10° | At 35° | At 10° | At 35° |
| Galena | 10.8 | 9.7 | | |
| Pyrite | 10.7 | 10.0 | 0.08 | 0.04 |
| Chalcopyrite | 12.7 | 10.9 | 0.87 | 0.13 |

The effectiveness of cyanide as a depressant for pyrite is amazing. For example, though contact is easily established in the absence of cyanide in a 25 mg. per liter ethyl xanthate solution at a pH value of 9, as little as 0.1 mg. per liter of sodium cyanide prevents contact. These tests were carried out in 20 c.c. of solution: consequently 0.001 mg. NaCN was sufficient to prevent contact with a pyrite specimen of which the total surface area was approximately 6 sq. cm. Direct flotation tests, carried out in stoppered cylinders, confirmed the extreme sensitiveness of pyrite to cyanide, but slightly more cyanide was necessary to prevent flotation. At a pH value of 9, flotation of pyrite was prevented by 0.5 mg. NaCN per liter when using 25 mg. per liter ethyl xanthate as collector and 20 mg. per liter terpineol as frother. Flotation was hindered but not completely prevented by 0.1 mg. per liter. We had hoped to study the abstraction of cyanide by pyrite but have been unable to find a sufficiently sensitive method of analysis. Its depressant action on pyrite, in fact, is the most sensitive test known for cyanide. We had hoped, also, to show by analytical methods that the depressant action of cyanide is due to its preventing adsorption of xanthate by the pyrite. The small amount of cyanide necessary to depress the pyrite, though it would consume a little iodine, was not expected to prevent the estimation of xanthate by iodine titration. However, this method proved unsuitable because of the liberation of considerable amounts of reducing ions by the alkali necessary to raise the pH value to such a value that small concentrations of cyanide are effective. No satisfactory method could be found for the estimation of xanthate in the presence of these ions or for its separation from them.

Nevertheless by taking advantage of the fact that xanthate is an excellent collector, even when in very low concentrations, it was shown that alkali and/or cyanide greatly reduced, and probably completely prevented, the abstraction of xanthate by pyrite. Four grams of pyrite was ground for 5 min. in a porcelain mortar with 50 c.c. of a 25 mg. per liter ethyl xanthate solution containing 10 mg. NaCN per liter, and at a pH value of 10. After standing for ½ hr. in contact with the very finely divided mineral the solution was filtered, and both the mineral and the solution were tested for xanthate. The *mineral* was washed and then placed in a 100 mg. per liter solution of pure m-cresol which is a frother having no collecting properties for pyrite. Over a range of pH value from 8 to 4 it showed no tendency to float, except for a surface film of the finest material. The *solution* was brought to a pH value of 7, and after the addition of 100 mg. per liter of m-cresol, it proved to be an excellent flotation medium for some freshly ground pyrite. A control test without the alkali and cyanide showed that pyrite abstracted so much of the xanthate that the filtrate was unable to cause flotation of freshly ground pyrite whereas the original pyrite, when washed and placed in a cresol solution, floated excellently. It may therefore be concluded that the depression of pyrite by alkali and/or cyanide is due to their ability to prevent adsorption of the xanthate by the mineral.

From Figs. 1 and 2, it is apparent that the differentiation between pyrite and chalcopyrite is less at 35° C. than at 10° C. Figs. 3 and 4 show that this is also true in the presence of copper sulphate. It follows that from this aspect the separation of chalcopyrite from pyrite should be carried out at as low a temperature as is consistent with plant requirements, bearing in mind that at the lower temperatures the speed of the conditioning processes may be considerably reduced.

In the presence of copper sulphate and cyanide, temperature changes have a profound influence on the response of pyrite to xanthate. At low temperatures the copper sulphate-cyanide solution acts as a depressant and an amazingly low concentration of cyanide is effective. The copper itself is not a depressant, for, in the absence of cyanide, the critical pH value is raised by it from 10.9 to 11.3. Nor is the cyanide ion responsible for prevention of contact, since at the lower pH values copper sulphate decreases the amount of cyanide necessary to prevent contact. A complex copper cyanide ion, therefore, seems to be the active depressant for pyrite at 10° C. At 35° C., however, copper sulphate is an activator for pyrite and the curve of Fig. 4 for pyrite does not differ greatly from the corresponding curve for sphalerite. It is apparent, therefore, that under the conditions of these experiments the pyrite-chalcopyrite and pyrite-sphalerite separations are more easily effected at low temperatures. On the other hand, if pyrite or arsenopyrite has to be floated in a circuit containing cyanide, an increase in temperature should be beneficial.

The main effect of raising the temperature to 35° having been to bring the curve for pyrite much closer to the curves for sphalerite and chalcopyrite, it was considered advisable to ascertain whether by raising the temperature still further, or by modifying the relative amounts of the reagents, the curves for the three minerals would become identical. However, we have found no conditions for which the curves are identical, nor have we obtained any evidence of the existence of such conditions.

It has been found previously that the amount of cyanide necessary to prevent contact with a sphalerite surface at any given pH value depends upon the ratio between the xanthate and copper sulphate additions (ref. 3, p. 275). The effect on the relative positions of the pyrite and sphalerite curves of varying the xanthate concentration, while keeping the copper sulphate addition constant, was therefore determined. Fig. 5 shows that 5 mg. per liter xanthate is insufficient, even at 35° C., to bring the curve for pyrite into the approximate region of the sphalerite curve; and, consequently, that even at this temperature the separation of sphalerite from pyrite would be possible by using minimal or "starvation" quantities of the collector. Conditions favorable for this separation, when copper sulphate and ethyl xanthate are used, are: (1) low temperature, (2) low xanthate concentration, and (3) a pH value between 6 and 8 if low temperature is impracticable. Low temperature and low xanthate concentration are not without effect on sphalerite flotation, but their influence on pyrite flotation is greater and therefore should be of value in selective flotation.

Fig. 6 shows that beyond 35° C. a further increase of temperature does not greatly increase the amount of cyanide necessary to prevent contact at a pyrite surface. At pH = 9 the maximum concentration of cyanide that can be tolerated without preventing contact is just under 80 mg. per liter at about 40° C. Fig. 4 indicates that at constant temperature the amount of cyanide that can be tolerated is almost independent of the pH value within the limits 7 to 11. It seems certain, therefore, that there is no temperature or pH value at which an amount of cyanide substantially in excess of 80 mg. per liter could be tolerated. With chalcopyrite, however, Fig. 4 shows that over 100 mg. per liter can be tolerated and with preactivated sphalerite (ref. 3, p. 276), 90 mg. per liter. We have not found any conditions under which pyrite can be preactivated by copper sulphate. However, for sphalerite and for pyrite that have not been preactivated, the *maximum* cyanide concentration is about 80 mg. per liter, and does not seem to differ very greatly for the two minerals. It has been found also that under one set of conditions the curves for sphalerite and stibnite are almost identical.[5]

It is of interest that whereas an increase of temperature from 10° to 35° raises the pyrite curve enormously, and the sphalerite curve slightly, it actually lowers the chalcopyrite curve slightly. However, as the curve for 35° C. is practically identical with that previously obtained at room temperature, it seems that there would be little further decrease at higher temperatures.

---

[5] Wark and Wark: *Jnl. Phys. Chem.* (1936) **40**, 799.

Thus the effect of temperature change on the chalcopyrite curves is in the same direction in the presence as in the absence of copper sulphate: this suggests that the cyanide concentration itself is the controlling factor, through its ability to prevent adsorption of xanthate. On the other hand, where an increase in temperature raises the curve (or moves it to the right), for example, with pyrite and sphalerite, it is suggested that the function of the cyanide is to control the copper-ion concentration and thus to control activation. Activation must precede adsorption of xanthate and the copper-ion concentration necessary for activation probably differs from mineral to mineral.

It had been found (ref. 3, p. 282, Fig. 10) that at room temperature with solutions containing amyl xanthate and cyanide, copper sulphate is not such an effective activator for sphalerite within the pH range 8 to 12 as on either side of this range. When it was found that copper sulphate became more effective as an activator for pyrite as the temperature was raised, it was decided to ascertain whether raising the temperature to 35° would result in any change in the sphalerite-amyl xanthate system. Comparison of the sphalerite curve of Fig. 7 with that of the earlier paper (ref. 3) indicates that though there remains a small region of poor response to xanthate, this region is much smaller at 35° C. The corresponding curve for pyrite and amyl xanthate is included in Fig. 7. At this temperature cyanide is not an effective depressant at pH values above 8, whereas at room temperature (ref. 3, p. 282, Fig. 9) a few milligrams per liter of cyanide effectively prevented contact at any pH value.

The results of the present investigation clear up some of the difficulties of previous work. Thus it was stated (ref. 2) that difficulty was experienced in fixing the lower left-hand portions of the pyrite and chalcopyrite curves, and that the former curve may have been 0.5 pH units in error. No such difficulty was experienced in determining the curves of Figs. 1 and 2, and it is probable that the earlier difficulty was due to lack of temperature control. It had been found (ref. 3, p. 287, Fig. 8) at room temperature that with 625 mg. per liter of ethyl xanthate present copper sulphate was within limits an activator for pyrite, as much as 40 mg. per liter of cyanide not preventing contact at pH = 9. This fact did not seem to fit in with the results for lower concentrations of xanthate and was inexplicable at the time. It is now apparent that the higher the xanthate concentration and the higher the temperature, the more likely is pyrite to float in the presence of copper sulphate and cyanide.

It had been shown (ref. 1) that the magnitude of the angle of contact is uninfluenced by temperature variations. The tenacity of air-mineral contact, therefore, is uninfluenced by temperature; provided, of course, that the temperature change does not prevent contact altogether.

The reasons for these effects of temperature on the formation of the xanthate film can only be considered in the broadest possible way. The factors that determine the direction and magnitude of any change of equilibrium with temperature are the heats of reactions of the various reactions involved. Since, however, there is not yet complete agreement concerning the nature of the reactions that occur, and moreover, we do not know the values of the heats of reaction (or adsorption) of the reactions in question, no progress can be made along these lines.

## SUMMARY

A study has been made of the influence of temperature on adsorption of xanthate at surfaces of galena, pyrite, arsenopyrite, chalcopyrite and sphalerite, and on the effects of alkali, cyanide and copper sulphate in hindering or promoting the adsorption. The development of a definite air-water-mineral contact angle has been used to indicate the adsorption of a xanthate film on the mineral surface.

1. In the absence of copper sulphate, a change in temperature from 10° to 35° merely alters slightly the amounts of depressants (cyanide and/or alkali) necessary to prevent contact, a greater concentration of depressant being necessary to prevent contact at 10° than at 35° C.

2. In the presence of copper sulphate, the influence of temperature on the amounts of cyanide and/or alkali necessary to prevent contact is slight for chalcopyrite and sphalerite, but is relatively great for pyrite and arsenopyrite. Under these conditions pyrite and arsenopyrite are much less influenced by the depressants at 35° C. than at 10° C.

3. The conditions most favorable for floating sphalerite away from pyrite are low temperature, low xanthate concentration, and if low temperature is impracticable, a small range of pH values which for the conditions used here is between 6 and 8.

4. The conditions most favorable for floating chalcopyrite or other copper-bearing sulphide minerals away from pyrite are likewise low temperature and low xanthate concentration.

5. There appears to be little advantage in raising the temperature of the system above 35° C. when pyrite or arsenopyrite is to be floated in the presence of copper sulphate and sodium cyanide.

6. The differentiation between sphalerite and pyrite when using amyl xanthate in a circuit containing copper sulphate and cyanide is much diminished as the temperature is raised.

## ACKNOWLEDGMENTS

The authors acknowledge gratefully the help they have received from the companies for which this work was carried out; viz., The Zinc

Corporation Ltd., Broken Hill South Ltd., North Broken Hill Ltd., Mt. Lyell Mining & Railway Co., Electrolytic Zinc Co. of Australasia Ltd., and The Burma Corporation Ltd.

They are especially indebted to Mr. H. Hey, under whose general direction the work has proceeded, for much helpful advice and criticism. Prof. E. J. Hartung has generously provided laboratory accommodation for the research in the Chemistry Department of the University of Melbourne.

## DISCUSSION

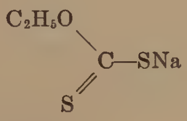
I. W. Wark and A. B. Cox (written discussion).—After publication of this paper, it was found that the curve of Fig. 3 for pyrite requires modification. There is a range of pH values from 6.2 to 7.8 for which no cyanide is required to prevent contact. From 7.8 to 11.3 a small amount of cyanide is required, with a sharp maximum of 20 mg. per liter at pH = 9.6. The mistake arose from considering too few solution compositions (17 were considered) in constructing the curve. Subsequent work with other collectors indicates that the corrected curve is typical for such systems; it illustrates the further development of the dip in the pyrite curve of Fig. 5.

# Principles of Flotation, VII—Mercaptobenzthiazole as a Flotation Agent

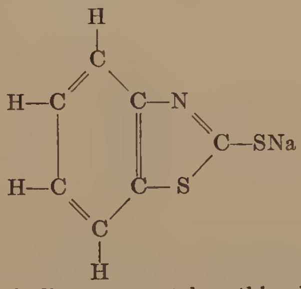
By Ian William Wark* and Keith Leonard Sutherland*

(New York Meeting, February, 1939)

Mercaptobenzthiazole and its sodium salt are marketed under the trade names Flotagen and Flotagen S respectively, for use as collectors for cerussite and other minerals. The structural formulas for sodium mercaptobenzthiazole and for sodium ethyl xanthate are:



Sodium ethyl xanthate



Sodium mercaptobenzthiazole

Chemically there is a resemblance between the two compounds, though the free acid (mercaptobenzthiazole itself) is much more stable than xanthic acid. Both are readily oxidized, e.g., by iodine to disulphides, and can be estimated by iodometric titration. Qualitatively they are similar as collectors in flotation, although there are quantitative differences between them that may be important in practice. It is deduced that the influence of the nitrogen atom is subordinated to that of the sulphur atoms, and that the dominant group of these compounds is the mercapto group —SH or —SNa.

The general method of investigation has been based on contact tests. Two temperatures, 10° and 35° C., have been chosen, and with a standard concentration of 20 mg. per liter of mercaptobenzthiazole (i.e., of the free acid) the influence of alkali, cyanide and copper sulphate on contact at sulphide mineral surfaces has been studied. This standard concentration corresponds to about 19 mg. per liter potassium ethyl xanthate; it brings out the differences between the minerals better than a higher concentra-

---

Manuscript received at the office of the Institute May 21, 1938. Issued as T. P. 1007 in Mining Technology, January, 1939.

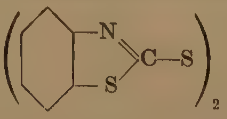
* Department of Chemistry, University of Melbourne, Melbourne, Australia.

tion would have done. The influence of alkalies on the amount of mercaptobenzthiazole necessary to induce contact at the surface of some oxidized minerals (malachite, anglesite and cerussite) was also investigated: the claim that the collector is a good one for cerussite is substantiated, but only for pH values below 8.

The effect of substituting copper acetate for copper sulphate was studied for the sulphide minerals. So interesting were the results that it has been decided to extend this phase of the work to include other copper salts and other collectors.

## Experimental Procedure

The methods used have been described in earlier communications.[3,4,8] In each test the clean polished mineral specimen was immersed in a solution prepared by adding the reagents in the order: (1) sodium carbonate and hydrochloric acid as necessary to buffer the solution and to give approximately the desired pH value, (2) sodium cyanide, (3) copper sulphate when necessary, (4) mercaptobenzthiazole, (5) a small amount of acid or alkali for the final adjustment of pH value. After ½ hr. the mineral was tested for an adsorbed collector film by bringing a bubble of air into apparent contact with the surface. If true contact (spreading) is possible, it occurs within ½ min. The surface was wiped with a linen pad before testing (to simulate the scrubbing action of the particles of the pulp) as has been found necessary previously to obtain consistent results. Figs. 1 to 5 show the relationship between the pH value and the cyanide concentration necessary to prevent contact: contact between mineral and air is possible below the curves and impossible above them. In Fig. 8, in which the critical pH value is plotted against the collector concentration, contact with the mineral is possible only above the curve for that mineral. Special methods of plotting have been used for Figs. 6, 7, 9 and 10.

The mercaptobenzthiazole was purified, before use, by repeated conversion into the sodium salt and back to the free acid, the former being water soluble and the latter practically insoluble. The free acid was finally crystallized from a hot 50 per cent aqueous alcohol solution. Large crystals were obtained, which melted sharply at 175° (uncorrected). Iodometric titration and estimation as the copper salt (see Spacu and Kuraš[2]) indicated a purity of 99.8 ± 0.2 per cent. A stock solution containing 400 mg. per liter of the collector was prepared by dissolving the free acid in N/40 NaOH. This solution is relatively stable, but oxidation to the disulphide 

proceeds slowly,

---

[3] References are at the end of the paper.

the oxidation in three days being 1 per cent. The copper acetate (C.P.) used was shown to be 99.9 per cent pure.

The temperature was controlled to within 1° of the specified value during the preparation of the solution, as well as during the period of immersion of the specimen. The pH value must be measured at the temperature of the test: one solution of pH value 11.3 at 10° showed a pH value of 10.8 at 35° C., alizarin yellow being the indicator for both determinations.

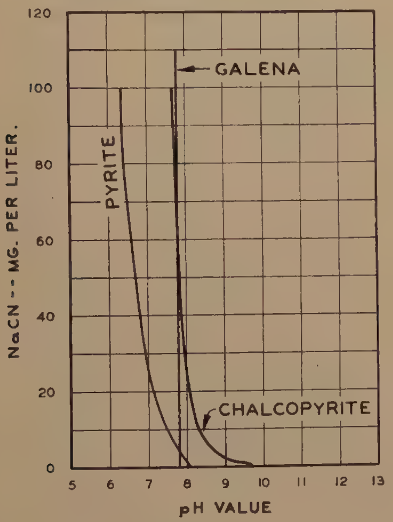


Fig. 1.

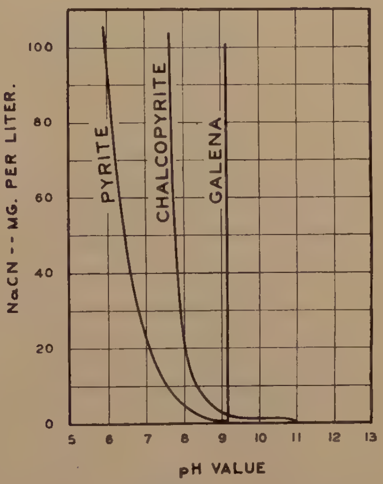


Fig. 2.

Fig. 1.—Relationship between concentration of sodium cyanide and pH value necessary to prevent contact at mineral surfaces.
$CuSO_4$, nil; mercaptobenzthiazole, 20 mg. per liter; temperature, 10° C.

Fig. 2.—Relationship between concentration of sodium cyanide and pH value necessary to prevent contact at mineral surfaces.
$CuSO_4$, nil; mercaptobenzthiazole, 20 mg. per liter; temperature, 35° C.

## Experimental Results

### *The Sulphide Minerals*

*No Added Copper Salts.*—Fig. 1 shows, for pyrite, chalcopyrite and galena, the relationship at 10° C. between the cyanide concentration and the pH value necessary to prevent contact. Sphalerite cannot be included, since it does not respond to the standard concentration of the collector within the range of pH values 4 to 13. The curves of Fig. 2, for 35°, are similar, but more alkali is required to prevent contact in the absence of cyanide.

*Copper Sulphate Present.*—Figs. 3 and 4, for 10° C. and 35° C., respectively, show the effect of an addition of 150 mg. $CuSO_4.5H_2O$ per liter. Comparison with Figs. 3 and 4 of the sixth paper of this series, in which corresponding curves are given for ethyl xanthate, indicates that:

1. At 35° the curves for chalcopyrite and sphalerite are in general similar for the two collectors. There are, however, small "islands" of noncontact in the mercaptobenzthiazole systems, the island for sphalerite being larger than that for chalcopyrite.

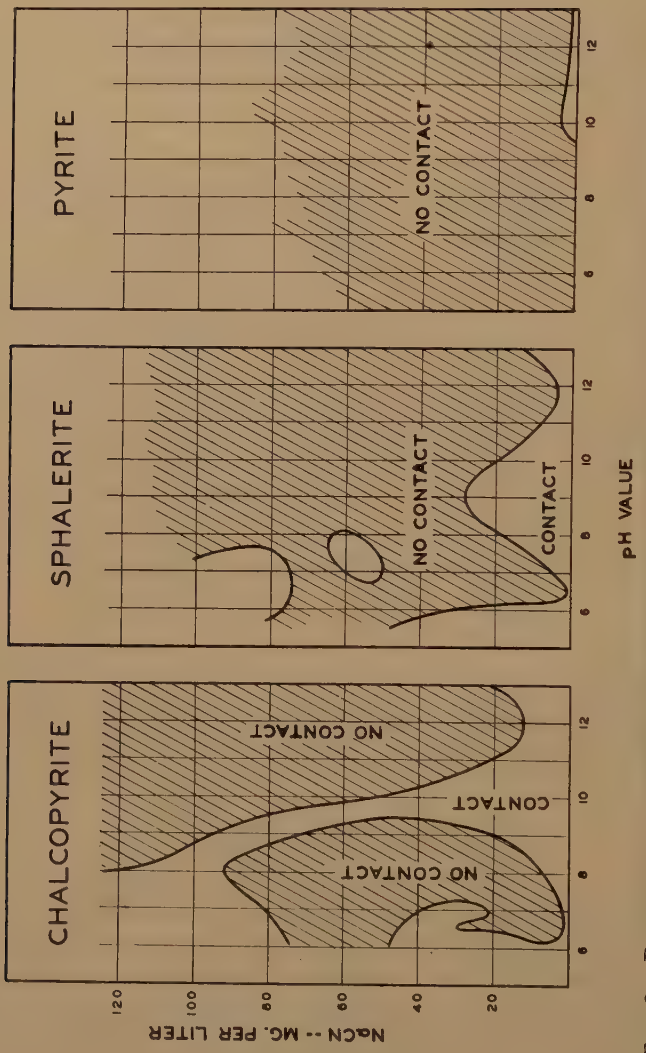


FIG. 3.—RELATIONSHIP BETWEEN CONCENTRATION OF SODIUM CYANIDE AND pH VALUE NECESSARY TO PREVENT CONTACT AT MINERAL SURFACES. $CuSO_4.5H_2O$, 150 mg. per liter; mercaptobenzthiazole, 20 mg. per liter; $Na_2CO_3$, 150 mg. per liter; temperature, 10° C.

2. Pyrite is more readily depressed if mercaptobenzthiazole is substituted for xanthate. In this system the second region of noncontact (the development of the island) is considerably larger.

3. On lowering the temperature from 35° to 10° the islands have considerably expanded in size for all the minerals. The second region

of depression has become more important than the first for sphalerite and pyrite.

It will be seen that even in the absence of cyanide there is, at 35° C., a small range of pH values for which contact with pyrite is impossible.

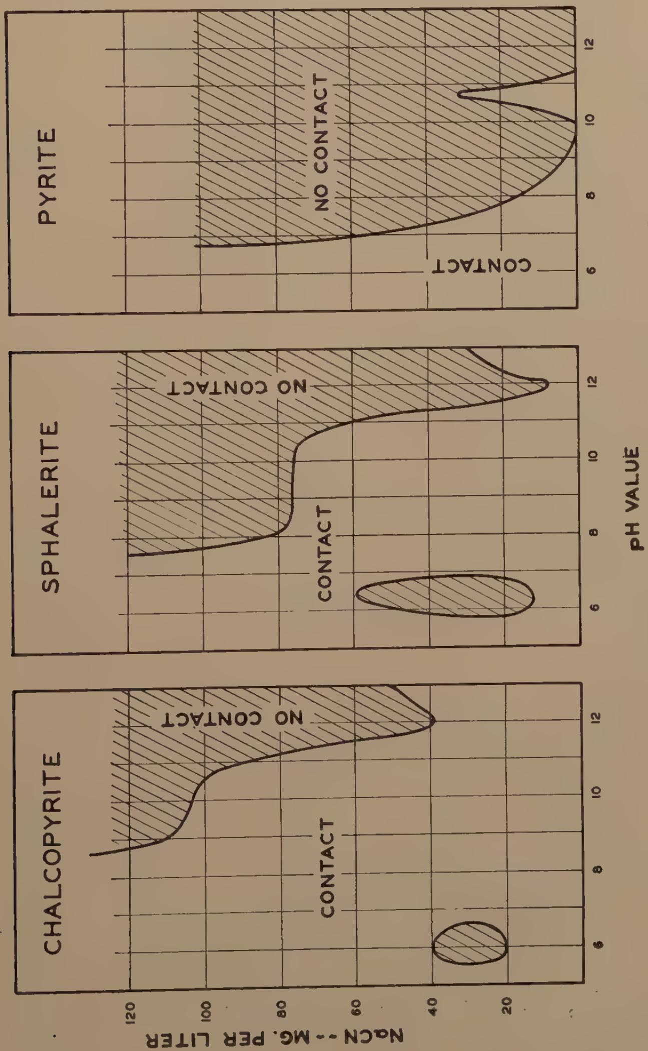


FIG. 4.—RELATIONSHIP BETWEEN CONCENTRATION OF SODIUM CYANIDE AND pH VALUE NECESSARY TO PREVENT CONTACT AT MINERAL SURFACES.

$CuSO_4.5H_2O$, 150 mg. per liter; mercaptobenzthiazole, 20 mg. per liter; $Na_2CO_3$, 150 mg. per liter; temperature, 35° C.

The dependence of this range on the concentration of the copper salt is shown in Figs. 6 and 7, the former being on a more open scale than the latter.

*Copper Acetate Present.*—Fig. 5 shows the effect of substituting for the copper sulphate of Fig. 4 an equivalent amount of copper acetate. The island region of noncontact has become more important.

### *Oxidized Minerals*

Fig. 8 shows the result of contact tests for three common oxidized minerals. Malachite and cerussite respond to relatively low concentrations of the collector. Flotation tests, in stoppered cylinders, are in agreement with the contact tests. For anglesite, since the consumption of the collector is high in both contact and flotation tests, and since high pH values (greater than 11) result in etching of the surface, the curve could not be determined very accurately. Within the limits of accuracy attained, the addition of 250 mg. per liter $Na_2CO_3$ did not influence the

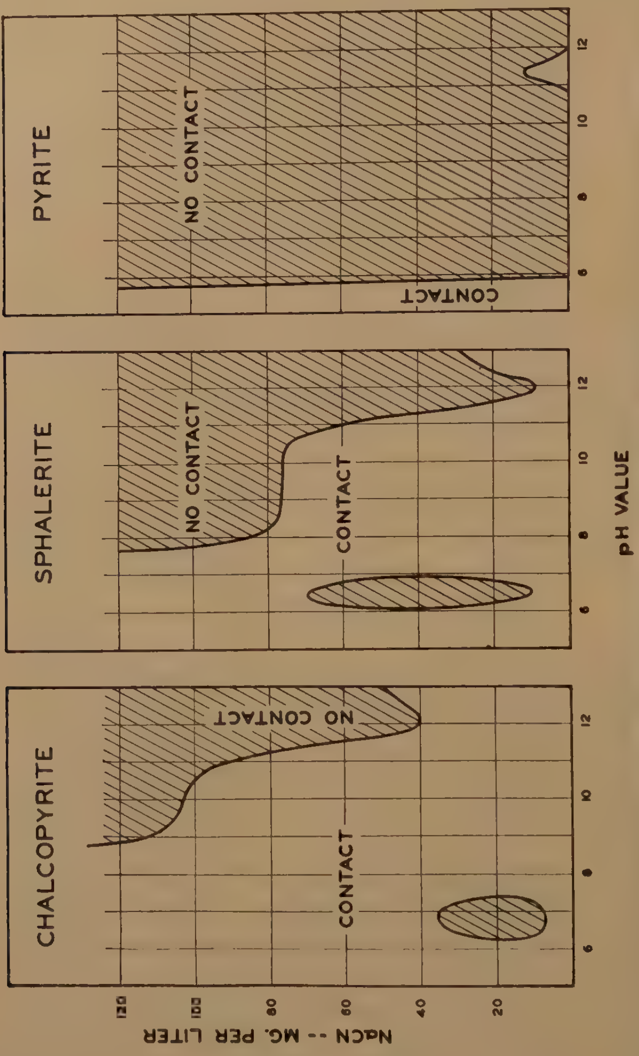


FIG. 5.—RELATIONSHIP BETWEEN CONCENTRATION OF SODIUM CYANIDE AND pH VALUE NECESSARY TO PREVENT CONTACT AT MINERAL SURFACES. $Cu(CH_3.CO_2)2H_2O$, 120 mg. per liter; mercaptobenzthiazole, 20 mg. per liter; $Na_2CO_3$, 150 mg. per liter; temperature, 35° C.

position of the curve, which is surprising because with xanthate as collector[6] carbonate did have an effect. The curve for anglesite is

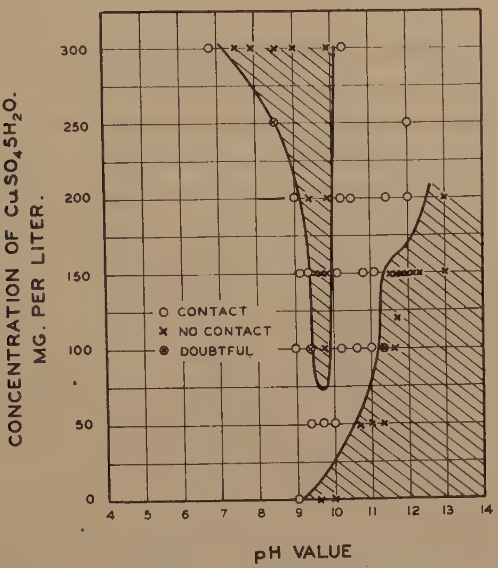


FIG. 6.—INFLUENCE OF CONCENTRATION OF COPPER SULPHATE ON pH REGION OF NO CONTACT FOR PYRITE.

Cyanide, nil; mercaptobenzthiazole, 20 mg. per liter; temperature, 35° C. Shaded areas are those of no contact.

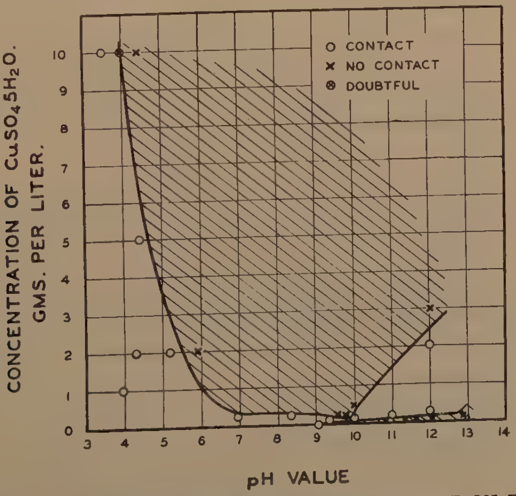


FIG. 7.—INFLUENCE OF CONCENTRATION OF COPPER SULPHATE ON pH REGION OF NO CONTACT FOR PYRITE.

Cyanide, nil; mercaptobenzthiazole, 20 mg. per liter; temperature, 35° C. Shaded areas are those of no contact.

unusual; increase of pH value usually increases the amount of collector required for contact. The reason for the exceptional behavior of anglesite may well be decreased consumption at high pH values, some of the lead ions reacting with alkali rather than with collector.

## Discussion of Results

The order of response of the minerals, in the absence of activators, is the same as for ethyl xanthate and other soluble sulphur-bearing collectors.[5] Cyanide is about equally effective in preventing contact whether ethyl xanthate or mercaptobenzthiazole is used, but alkali is more effective with the mercapto compound. The effect of temperature changes is small for chalcopyrite and pyrite, but the critical pH value for galena is raised by about one pH unit in changing from 10° to 35°. (It is lowered a similar amount when using ethyl xanthate.)

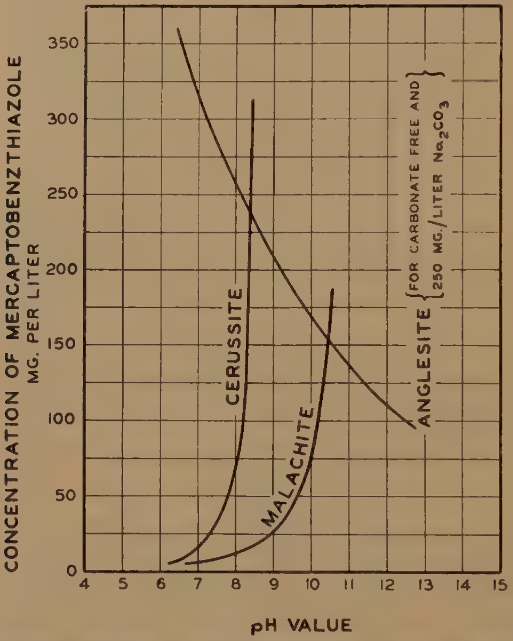


FIG. 8.—Relationship between concentration of mercaptobenzthiazole and pH value necessary to prevent contact. (Contact possible above curves.) Temperature, 35° C.; $Na_2CO_3$, nil; NaCN, nil.

Copper sulphate changes the type of the curves and temperature becomes more important. At 35° there is the standard type of curve for chalcopyrite and sphalerite,[5] but there is, in addition, the island of noncontact referred to above. The standard portion is determined primarily by the components other than the collector, for its form coincides with that of the lines of equal potential of a copper electrode in collector-free solutions.[4] It has been shown elsewhere that this type of curve results from the production of complex cupricyanide by the added cyanide, no free cyanide being available for preventing contact until all the copper has been converted into the complex.

Subsequent work has shown that similar islands of noncontact can be obtained in xanthate solutions if the collector concentration and temperature are low. Consideration of their nature will be deferred until this work is described.

At a pH value of 11 the alkali seems to assume the dominant role as depressant, presumably because it prevents adsorption of the collector by the activated mineral, or (with chalcopyrite) by the mineral itself. At pH = 12, a curious change occurs in the solution, for the curves of Fig. 4 turn upward. Obviously either the depressant power of the solution is lowered or its activating power is raised. We know from the study (already referred to) of the potential of a copper electrode in collector-free solution that this change occurs in the absence of collectors. We know also, from the work of Pickering,[1] that alkalies tend to dissolve basic salts of copper, and it seems probable that the two phenomena are related.

Since the copper sulphate is almost invariably added to alkaline solutions, the greater part of the copper is precipitated as basic carbonate or basic sulphate. The nature of the precipitate governs the final condition of the solution: consequently it may be important in flotation. Substitution of other copper salts for the sulphate may therefore be expected to alter the position of the curves, and possibly to lead to better differentiation. Experiment confirms this expectation. Fig. 5 shows that copper acetate greatly increases the differentiation between pyrite and sphalerite or chalcopyrite.

At 35° C. no cyanide is required to depress pyrite over a range of pH values from 6 to 11, so that separations should be easily accomplished at this temperature. One would anticipate a much greater margin of safety with this reagent combination than with any other that we have studied, but whether the combination is economic in practice remains to be determined.

There are several different basic carbonates and sulphates of copper, and the concentrations and relative proportions of the precipitate determine which of these compounds form. The influence of an increase in copper sulphate concentration was therefore determined for pyrite, it being considered that a higher concentration would produce an effect similar to that produced by copper acetate. Instead of determining the usual type of curve for a number of different concentrations of the sulphate, only the interesting region of noncontact in the absence of cyanide was studied. Fig. 6 shows the effect of increasing the concentration of the copper salt to 300 mg. per liter and Fig. 7, on a less open scale, of increasing the concentration to 10 grams per liter. With 1.5 grams per liter of the sulphate, the conditions are very similar to those with 120 mg. per liter of the acetate (Fig. 5), there being no need to add cyanide to prevent contact within the pH range 6 to 11. The conditions are not identical above pH = 11, however, for with the acetate no cyanide need be added to prevent contact beyond 12, whereas with the sulphate the cyanide is necessary to at least 13, and probably for all pH values above 11.

Whether higher copper sulphate concentrations would have an appreciable effect on the curves for sphalerite and chalcopyrite has not been determined. However, predictions concerning differential flotation under such conditions are unnecessary, for such high concentrations could have little value in practice.

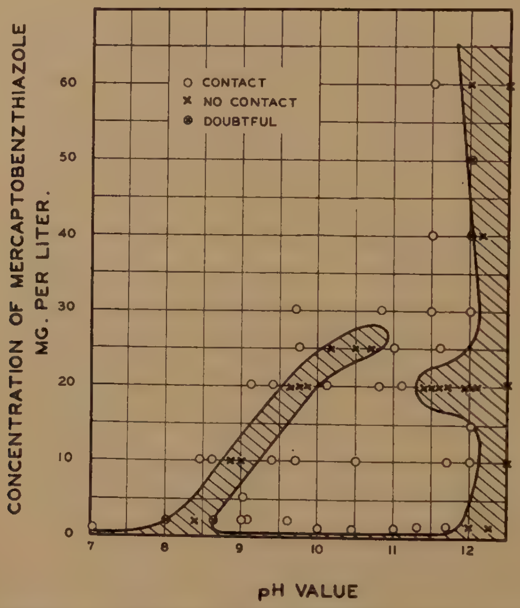


FIG. 9.—INFLUENCE OF CONCENTRATION OF MERCAPTOBENZTHIAZOLE ON pH REGION OF NO CONTACT FOR PYRITE.

Cyanide, nil; $CuSO_4.5H_2O$, 150 mg. per liter; temperature, 35° C. Shaded areas are those of no contact.

Two other figures, 9 and 10, show the dependence of the extent of the region of noncontact for pyrite (in the absence of cyanide) on the collector concentration and on the temperature respectively. These figures present empirical knowledge, for which no explanation can be offered. Fig. 9 indicates that a decrease in collector concentration would have little influence on the width of the available pH range for depression of pyrite, which is about one unit for any concentration below 25 mg. per liter. (The region above 11 can be neglected because sphalerite also would probably be depressed).

Fig. 10 indicates that temperature control is important. For example, at a pH value of 9, contact (and presumably flotation under the specified conditions) would be impossible below 17°, possible from 17° to 22°, impossible again from 22° to 35°, and thereafter possible again.

It is likely that the curves obtained for pyrite with mercaptobenzthiazole as collector are typical of those obtainable with other collectors of the xanthate type, provided they are used in suitable concentration and at the correct temperature. This suggestion is being tested, using ethyl xanthate as collector. Corresponding curves for sphalerite and chalcopyrite will also be determined in an endeavor to determine the best conditions for differential flotation.

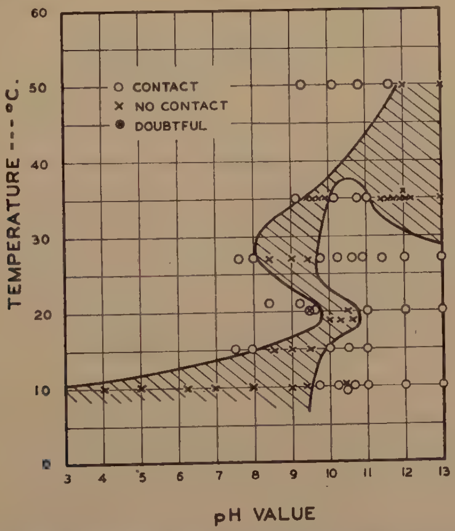


Fig. 10.—Influence of temperature on pH region of no contact for pyrite. Cyanide, nil; $CuSO_4.5H_2O$, 150 mg. per liter; mercaptobenzthiazole, 20 mg. per liter. Shaded areas are those of no contact.

## Summary

The influence of alkalies, cyanide and copper sulphate on the adsorption of the collector mercaptobenzthiazole (Flotagen) by the minerals galena, sphalerite, pyrite and chalcopyrite has been investigated for the two temperatures 10° and 35°. The captive-bubble method has been used to test for adsorption.

In the absence of copper sulphate the minerals respond to this collector in the same order that they respond to ethyl xanthate.

In the presence of copper sulphate there is excellent differentiation between pyrite and chalcopyrite, and between pyrite and sphalerite. There is a relatively wide range of pH values over which no cyanide is required to prevent adsorption on pyrite. The dependence of this pH range on the temperature, on the concentration of the copper sulphate, and on the concentration of the collector, has been studied.

The substitution of copper acetate for copper sulphate greatly increases the differentiation between pyrite and chalcopyrite and between pyrite and sphalerite. Other anions and the acetate are to be investigated with ethyl xanthate.

Cerussite and malachite adsorb mercaptobenzthiazole from solutions of low concentrations, provided that free alkali is not present. On the other hand, anglesite responds more readily in alkaline solutions, but relatively high concentrations are required.

## Acknowledgments

The authors desire to express their thanks for the help they have received from the companies for which this work was carried out; viz., The Zinc Corporation Ltd., Broken Hill South Ltd., North Broken Hill Ltd., Mt. Lyell Mining and Railway Co., Electrolytic Zinc Co. of Australasia Ltd., and the Burma Corporation Ltd.

They are especially indebted to Mr. H. Hey, under whose general direction the work has proceeded, for continuous help and encouragement. Prof. E. J. Hartung has generously provided accommodation for the research in the Chemistry Department of the University of Melbourne.

## References

1. S. U. Pickering: *Jnl.* Chem. Soc., (1909) **95,** 1409.
2. G. Spacu and M. Kuraš: *Ztsch. anal. Chem.* (1935) **102,** 24.
3. I. W. Wark and A. B. Cox: *Trans.* A.I.M.E. (1934) **112,** 189.
4. I. W. Wark and A. B. Cox: *Trans.* A.I.M.E. (1934) **112,** 245.
5. I. W. Wark and A. B. Cox: *Trans.* A.I.M.E. (1934) **112,** 267.
6. I. W. Wark and A. B. Cox: Page 7, this volume.
7. I. W. Wark and A. B. Cox: Page 41, this volume.
8. I. W. Wark and A. B. Cox: *Eng. and Min. Jnl.* (1936) **137,** 641.

# Conditioning Surfaces for Froth Flotation

By James E. Norman* and Oliver C. Ralston,† Member A.I.M.E.

(New York Meeting, February, 1939)

Separation of minerals by froth flotation is rightly called an art. It can truthfully be said that no two ores separate in the same way. The difference in results obtained when natural and synthetic mixtures of minerals are separated is so great that such tests frequently have been worthless in attempting to select conditions in which a natural mixture will separate. With a few rare exceptions, the natural mixture is much more difficult to treat than a synthetic mixture, and a much poorer separation is obtained.

Perhaps several experimenters have wondered why 10 or 20 per cent of a mineral being floated from an ore does not float and is different from the 90 or 80 per cent that is recovered. In experimental tests on pure sphalerite, observers[1] have noted that varying amounts of sphalerite may be froth-floated with pine oil alone, the amount recovered in the froth depending apparently upon the source of the sulphide.

The only explanation of results such as these, barring insufficiency of frother or time of flotation, is that the surface of the mineral floated is different from that of the mineral depressed. This difference often has been found to be caused by natural contamination of mineral surfaces, apparently brought about by weathering and exposure to natural solutions. There is virtually no rock that is absolutely unweathered.

One of the writers had an exceedingly instructive experience in 1931 while working with United Verde copper-zinc iron sulphide ore in Arizona. Nonselective flotation of chalcopyrite and sphalerite away from some of the pyrite was all that could be accomplished. All known depressants produced only slight effect. Sodium cyanide showed some effect, but so much had to be used that only a small amount of chalcopyrite could be

---

Published by permission of the Director, Bureau of Mines. Manuscript received at the office of the Institute Jan. 5, 1939. Issued as T. P. 1074 in Mining Technology, May, 1939.

* Junior Chemical Engineer, Bureau of Mines, Eastern Experiment Station, College Park, Md.

† Chief Engineer, Nonmetals Division, Bureau of Mines.

[1] A. W. Fahrenwald and J. Newton: Sphalerite—A Study, Part 2. *Eng. and Min. Jnl.* (1938) **139**, 44.

Also G. H. Buchanan and L. J. Christman: Effect of Certain Chemicals on the Floatability of Galena and Sphalerite. American Cyanamid Co., *Tech. Paper* No. 9 (1927) 6.

floated free when xanthate collectors were used. An inspiration led to a test in which excess cyanide was added and then removed and the pulp washed. This leached pulp permitted very effective separation of chalcopyrite containing most of the silver and gold of the ore. The sphalerite would not float until activated with copper sulphate. Investigation proved that the cyanide leach cleaned off films of chalcopyrite from the sphalerite and pyrite and also cleaned up the silver and gold minerals. The effects of this chemical cleaning, coming at the end of many months of discouraging failure, seemed little short of miraculous. Similar remarkable effects in separation of nonmetallic minerals are to be discussed later in this paper.

## Methods of Cleaning Mineral Surfaces

Cleaning of the dirty surfaces of minerals has allowed much better separations to be made by subsequent flotation. For some minerals, only mild treatment is required to produce good separation. Wet grinding, for instance, will be effective on most ores. With others, however, separation cannot be achieved by flotation when the usual methods of preparation are used. Two general methods of cleaning contaminated surfaces have been developed: (1) chemical preparation, (2) attrition milling.

## Chemical Preparation

Chemical preparation consists in washing the flotation feed with solutions of dispersing and/or metal-ion complexing reagents such as hydrofluoric acid, phosphoric acid, fluosilicic acid, sodium hydroxide, tetrasodium pyrophosphate or sodium cyanide. These chemicals tend either to complex metal ions or to disperse slime adhering closely to mineral surfaces. Hydrofluoric acid has given the best results in most tests, because of its ability to complex several metal ions and to "loosen" slime. When this acid is excessive it forms un-ionized compounds with the chief offenders, the $Al^{+++}$ and the $Fe^{+++}$ ions, as well as several others. It is known that the $Al^{+++}$ and $Fe^{+++}$ ions will activate silicates that will not float in soap solutions and cause them to be filmed by soap. In addition, these ions will cause partial depression of several silicates to cationic collectors, especially in acid circuit, when complete flotation of the silicates is expected. The removal of these ions, as would be expected, allows better separation. Hydrofluoric acid also disperses slime from the surface of contaminated minerals. This action is not confined to silicate slime but has been noted with any mineral covered with fines. A striking example of this phenomenon was observed upon adding hydrofluoric acid to a slurry of iron-stained kyanite that had been washed entirely free of any liberated slime. Upon the addition of the acid, the slurry almost instantly became highly turbid with red iron oxide.

## CLEANING BY ATTRITION MILLING

The second method of cleaning surfaces consists in rubbing slime from the surface of mineral grains by means of an attrition grinder. This machine (Figs. 1 and 2) is merely a highly efficient agitator, which causes numerous collisions of particles in a slurry and the attendant rubbing and scraping of surfaces. When satisfactory cleaning is not obtained with the slurry of flotation feed alone, a hard, heavy grinding medium, such as garnet or zircon of suitable size, is added. This grinding aid is later tabled out of the granular part of the flotation feed.

## RESULTS OF SURFACE CLEANING

The peculiar behavior of sphalerite was noticed during work with an ore from Rosiclair, Ill., that contained sphalerite, fluorspar, calcite, quartz, and a small amount of galena. When the ore was ground to liberation at 65 mesh and froth was floated with pine oil alone, 15 to 20 per cent of the sulphides went into the concentrate. When the ore was treated in the attrition mill and deslimed before flotation, the recovery of sphalerite was almost complete. To study this peculiar occurrence further, the sulphide fraction of the ore from a table separation was washed thoroughly with water and divided into three parts. The first was floated with pine oil, and 93 per cent of the sphalerite was in the concentrate. The second was washed with 5 per cent HF solution, then washed free of acid. Intense flocculation of the sphalerite was noticed as soon as the acid was added. This fraction gave a recovery of 99+ per cent of the sulphides when floated with pine oil. The third portion

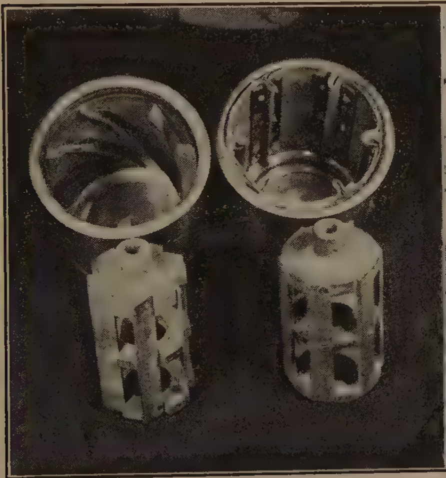


FIG. 1.—ROTOR AND STATORS: NO. 1 ON LEFT; NO. 2 ON RIGHT.

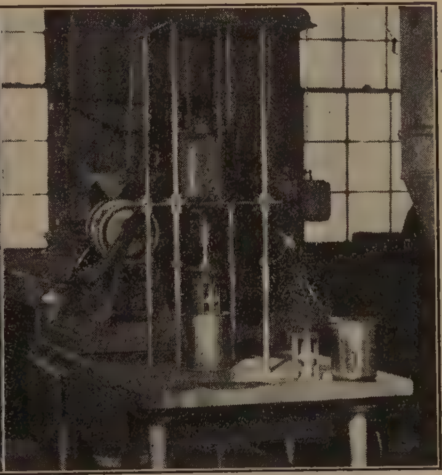


FIG. 2.—ATTRITION-MILL ASSEMBLY.

was washed with 5 per cent NaCN solution and washed free of cyanide. When floated with pine oil, 99+ per cent of the sphalerite was recovered. Thus, sphalerite was only partly floatable before being cleaned but completely floatable after cleaning.

A vermiculite rock from Libby, Mont., was tested for removal of silicate gangue. The gangue was composed essentially of green diopside with fibrous tremolite grading into actinolite, quartz, and feldspar. The minus 14 plus 20-mesh fraction was put across a concentrating table for the purpose of washing off slime. The washed crude was then treated with the following reagents:

| | Lb. per Ton | | Lb. per Ton |
|---|---|---|---|
| Armour Co. mixed amines, AM-1180, as hydrochloride | 0.25 | $H_2SO_4$ | 2.5 |
| Crude petroleum oil | 5.5 | $Al_2(SO_4)_3.18H_2O$ | 2.5 |

When these reagents had been added, a small amount of very fine material, heavily coated with oil, floated to the surface of the slurry and was deposited on the sides of the pan in which the slurry was conditioned. Upon being passed over a concentrating table, none of the coarse material was agglomerated and there was no separation. When the charge was re-treated with the reagents given below, agglomeration and separation was obtained and the products were as follows:

| Reagents | Rougher, Lb. per Ton | Scavenger, Lb. per Ton | Reagents | Rougher, Lb. per Ton | Scavenger, Lb. per Ton |
|---|---|---|---|---|---|
| Mixed amines AM-1180, as hydrochloride | 0.25 | | $H_2SO_4$ | 2.5 | 1.25 |
| Crude oil | 5.5 | 1.4 | $Al_2(SO_4)_3.18H_2O$ | 2.5 | 1.25 |

| Products | Weight, Per Cent | Vermiculite, Per Cent |
|---|---|---|
| Combined concentrates | 47.5 | 89. |
| Tailing | 52.5 | 3.5 |

After removal of slimes, by the reagents themselves in this case, good separation was attained. By treating a fraction of the same size 2½ min. at 50 per cent solids in the attrition mill and washing on a 20-mesh sieve before treatment with the reagent combination listed above, agglomeration was obtained the first time across the table with the following products: combined concentrates 57 per cent by weight containing 93 per cent vermiculite; tailing 43 per cent by weight containing 1 per cent vermiculite.

Some of the loosely bound granular gangue was broken down by attrition milling and discarded through the 20-mesh sieve, thus increasing the vermiculite content of the feed.

Another fraction was washed with 2 per cent HF solution and then washed free of fines on a 20-mesh sieve. When treated as above with reagents and tabled, the following products were obtained: combined concentrates, 52.5 per cent by weight containing 94.5 per cent vermiculite; tailing 47.5 per cent by weight containing 1.5 per cent vermiculite.

This reagent combination of a long-chained amine, an acid, and the salt of a trivalent metal may be said to be a general method of separating micas from granular silicates. The trivalent salt, especially that of aluminum, prevents granular silicates from being filmed by cationic collectors and exerts little effect on the micas. Muscovite, vermiculite, phlogopite and lepidolite have been concentrated in this manner, but biotite is an exception.

A sample of phosphate rock (washery tailings) from the Southern Phosphate Corporation's Sand Gully washery near Bartow, Fla., was screened on 42 mesh and the undersize was froth-floated. The rock consisted essentially of quartz and phosphate rock. The flotation feed was rather coarse, as nearly all of it is larger than 100 mesh. The sample was washed thoroughly with water to remove free slime. Quartz was floated from phosphate and reagents used were: cetyl trimethyl ammonium bromide (Dupont) with 0.24 lb. rougher per ton; pine oil, with 0.12 lb. rougher per ton. The following products were obtained: quartz concentrate, 79.1 per cent by weight containing 2.7 per cent bone phosphate of lime; tailing, 20.9 per cent by weight containing 55 per cent B.P.L.

Another sample of the same material was washed with water to remove slime and was then treated for 2 min. in the attrition mill (stator No. 2) at 67 per cent solids. One per cent on the weight of the feed was slimed. This slime was found by microscopic examination to consist of clay, calcium phosphate and quartz. The attrition-mill product was then froth-floated with cetyl trimethyl ammonium bromide (Dupont), 0.12 lb. rougher per ton and pine oil, 0.12 lb. rougher per ton. These products were obtained: quartz concentrate, 84.5 per cent by weight containing 2.0 per cent B.P.L., and tailing, 15.5 per cent by weight containing 73 per cent B.P.L.

Here the removal of 1 per cent of the weight of the feed as (attrition) slime greatly improved the separation and allowed the use of only half the amount of collector previously used. This washery tailing is well suited to quartz flotation because it is relatively free from slime, but slime that cannot be removed by a simple water wash must be removed to secure the best results.

A crude magnesite rock from Chewala, Wash., was tested for the removal of silica. The rock carried 5.48 per cent $SiO_2$ and the gangue was principally talc and serpentine with a small amount of quartz. The talc and serpentine were present mostly as middling particles, as smears or thin sheets of gangue on magnesite particles, or as inclusions in the magnesite.

It was desired to reduce the silica content of the crude rock to less than 3.5 per cent. The rock was crushed and rolled past 20 mesh and divided into the following fractions by screening and settling:

| Fraction | Weight, Per Cent | $SiO_2$, Per Cent |
|---|---|---|
| −20 +48 mesh | 49.3 | 5.04 |
| −48 mesh +20 microns | 49.7 | 5.52 |
| −20 microns | 1.0 | 20.6 |

The minus 20 plus 48-mesh fraction was agglomerate-tabled with the following reagents: cetyl trimethyl ammonium bromide, 0.24 lb. per ton; crude oil 6.0 lb. per ton. The results of this separation were as follows:

| Products | Weight, Per Cent | $SiO_2$, Per Cent |
|---|---|---|
| Concentrate | 29.5 | 9.19 |
| Tailing | 70.5 | 3.16 |

The minus 48-mesh fraction was froth-floated with the following reagents:

| Reagents | Talc Rougher, Lb. per Ton | Talc Cleaner, Lb. per Ton | Silica Rougher, Lb. per Ton |
|---|---|---|---|
| Pine oil | 0.16 | 0.16 | |
| Cetyl trimethyl ammonium bromide | | | 0.32 |

The middling fraction from the talc cleaner was recombined with the tailing from talc rougher to form the slurry for silica rougher. The products were:

| Products | Weight, Per Cent | $SiO_2$, Per Cent |
|---|---|---|
| Talc concentrate | 11.1 | 14.7 |
| Silica concentrate | 17.4 | 10.3 |
| Tailing | 71.6 | 2.80 |

The slime fraction was discarded. Upon mixing of magnesite concentrates from agglomerate tabling, a product containing 2.98 per cent

$SiO_2$ was obtained, with a recovery of 70.4 per cent of the feed. The same magnesite rock was treated in the attrition mill for 10 min. with 20 per cent of the weight of magnesite of minus 35 plus 65 mesh zircon as abrasive. The plus 100-mesh fraction was removed and tabled to remove zircon, and then recombined with the fines. The magnesite was separated into these fractions:

| Product | Weight, Per Cent | $SiO_2$, Per Cent |
|---|---|---|
| −20 + 48 mesh | 41.3 | 3.81 |
| −48 mesh + 20 microns | 45.4 | 2.90 |
| −20 microns | 13.3 | 18.5 |

Here, by combining the two coarser fractions, a magnesite product of satisfactory purity could be obtained. The silica content is 3.33 per cent and the recovery of the feed is 86.7 per cent.

To further study the separation, the products were treated as above with the same reagent combinations. Here the amount of collector required could not be reduced appreciably. Flotation apparently depended on the concentration of collector in the slurry, as a large amount was required to start the separation and very little more to give complete recovery of all the material that would float. The products obtained by agglomerate tabling and froth flotation of the coarse and fine fractions, respectively, were:

| Products | Agglomerate Tabling | | Flotation | |
|---|---|---|---|---|
| | Weight, Per Cent | $SiO_2$, Per Cent | Weight, Per Cent | $SiO_2$, Per Cent |
| Talc concentrate | | | 3.4 | 13.3 |
| Silica concentrate | 7.6 | 10.5 | 8.8 | 10.6 |
| Tailing | 92.4 | 3.15 | 87.6 | 1.71 |

Combination of the two magnesite fractions results in a magnesite product of 2.42 per cent $SiO_2$, with a recovery of 77.6 per cent of the feed.

Attrition grinding to reduce the size of the softer gangue here allows a suitable product to be made by the grinding alone or a better product by subsequent concentration. The latter is superior in quality to that obtained by concentration alone, while both show a greater recovery than is obtained by concentration alone.

Microscopic examination of the magnesite concentrates showed that the remaining gangue occurred chiefly as inclusions in magnesite grains.

It should be mentioned that the attrition milling was carried out in a brass-lined stator and a small amount of sodium cyanide had to be added to agglomeration and flotation slurries to prevent activation and flotation of magnesite apparently by copper. Otherwise, magnesite is not floatable by a quaternary ammonium base or its salts. It may be stated as a general rule that a quaternary ammonium base or its salts is the proper type of reagent for floating quartz or granular silicates from nonsilicates. These reagents generally have only a slight tendency to film nonsilicates, while with the long-chained amines (which are also silicate floaters) this tendency is much more pronounced.

Talc rock from the Old Dump, Arnold mine, of the Loomis Talc Co. of Gouverneur, N. Y., was tested for removal of impurities. The principal impurity was tremolite (of about 12.5 per cent CaO content), and there was some serpentine and a small amount of calcite.

Talc should be easily separable from these impurities, but this rock contained middling particles of tremolite partly altered to fibrous talc. As a result considerable tremolite is concentrated with the talc when it is froth-floated. The highest recovery and grade of talc concentrate by ordinary grinding methods was obtained by grinding in a pebble mill with dispersant, desliming, froth-floating and cleaning the rougher concentrate twice, then regrinding the cleaner concentrate and recleaning. The following reagent was used and gave these results:

| Reagent | Rougher, Lb. per Ton | Cleaner 1 | Cleaner 2 | Cleaner 3 |
|---|---|---|---|---|
| Di-n-butylamine (Sharples Solvent Co.) | 0.48 | 0.12 | 0.12 | 0.12 |

| Products | Weight, Per Cent | CaO, Per Cent |
|---|---|---|
| Talc cleaner concentrate | 30.4 | 1.63 |
| Slime, middlings and tailing | 69.6 | 11.26 |

Omitting the regrinding of the talc concentrate in the pebble mill and substituting a 10-min. attrition grind, with garnet approximately equal in weight to the talc, in a 50 per cent solids slurry, gave the following results:

| Products | Weight, Per Cent | CaO, Per Cent |
|---|---|---|
| Talc cleaner concentrate | 28.5 | 1.24 |
| Slime, middling and tailing | 71.5 | 11.20 |

The particle size of the talc was considerably reduced, and it was noticed that the talc fibers were torn apart or "micronized."

The collector di-n-butyl amine has been compared with several other collectors of the cationic type of talc and has been found to give the most efficient separation. Other short-chained amines, notably diamyl amine, are also effective. It may be stated as a general rule that a hydrous silicate containing 5 per cent or more of water of hydration is floatable with the short-chained amines. Talc, pyrophyllite, sericite, clays, and weathered mica fall in this class. Unaltered muscovite, which contains a theoretical 4.5 per cent water of hydration, is floatable with these collectors only when large quantities are used in an acid circuit.

The separation of pyrophyllite rock has likewise been improved by attrition milling. The pyrophyllite tested was from Staley, N. C., and contained quartz as gangue. The rock was ground to pass 48 mesh and froth-floated with pine oil, rougher 0.50 lb. per ton and cleaner 0.25 lb. per ton. The results were:

| Products | Weight, Per Cent | $Al_2O_3$, Per Cent |
|---|---|---|
| Concentrate | 72.0 | 23.7 |
| Tailing and middling | 28.0 | 0.59 |

When the feed was attrition-milled for 10 min. with 50 per cent solids these results were obtained:

| Products | Weight, Per Cent | $Al_2O_3$, Per Cent |
|---|---|---|
| Concentrate | 62.0 | 26.9 |
| Tailing and middling | 38.0 | 0.54 |

Pine oil proved to be a satisfactory collector. This is true when the pyrophyllite is predominantly coarse. However, when pyrophyllite is finely divided pine oil as a collector is markedly inferior to the short-chained amines.

A residual kaolin, from Nelson County, Virginia, was tested to remove the remaining partly altered feldspar from the kaolinite.

The feed was treated with diamyl amine (Sharples Solvent Co.), rougher 1.1 lb. per ton and 0.55 lb. per ton of cleaner 1 and of cleaner 2. Results of the separation were:

| Products | Weight, Per Cent | Grade, Per Cent |
|---|---|---|
| Concentrate | 77.0 | 37.5 $Al_2O_3$ (95 kaolin) |
| Tailings and middlings | 23.0 | 25.7 $Al_2O_3$ (27 kaolin) |

When the feed was attrition-milled for 15 min. with 50 per cent solids and floated as before the results were:

| Products | Weight, Per Cent | Grade, Per Cent |
|---|---|---|
| Concentrate | 81.6 | 37.2 $Al_2O_3$ (92 kaolin) |
| Tailing and middlings | 18.4 | 23.1 $Al_2O_3$ (12 kaolin) |

More of the coarser kaolin, which was not floatable before, went into the concentrate after attrition milling.

It should be noted that in the flotation of the hydrous silicates a stiff, voluminous froth is obtained and that separations are better if pulp density is low. Twelve and one-half per cent of solids has proved satisfactory. With the attrition-ground sample the kaolin was ground finer, resulting in a stiffer froth. More gangue was entrapped, therefore the concentrate from the attrition-treated sample was slightly lower in grade. This could be prevented by separation of very fine clay by sedimentation.

The attrition mill has been used to abrade iron stain from glass sand and has resulted in a marked lowering of the ferric oxide content of the sand. This method has been applicable to every stained sand tested. Results are given on three glass sands, from Jean, Nev., Butler, Pa., and Millville, N. J.

The Jean (Nev.) and Butler (Pa.) sands were attrition-milled for 15 min. at 67 per cent solids with 20 per cent of their weight of minus 35 plus 65-mesh garnet, and the garnet was removed after treatment by tabling. A portion of the table product was magnetically separated to remove high-iron particles. The results of these tests were:

| Sand | $Fe_2O_3$, Per Cent | | |
|---|---|---|---|
| | In Crude | In Attrition-milled Table Product | In Attrition-milled Table Product, Nonmagnetic |
| Jean (Nev.) | 0.12 | 0.07 | 0.046 |
| Butler (Pa.) | 0.20 | 0.11 | 0.054 |

The Millville (N. J.) sand was attrition-milled for 10 min. at 67 per cent solids with 30 per cent of its weight of minus 35 plus 65-mesh zircon. The zircon was removed by tabling, and part of the table product was magnetically separated. Another sample was treated in like manner, except that the abrading medium was omitted. The results, expressed in $Fe_2O_3$ contents remaining, were:

| Sand Product | Washed, Per Cent | Nonmagnetic, Per Cent |
|---|---|---|
| 1. Crude | 0.28 | 0.058 |
| 2. Attrition-milled without zircon | 0.25 | 0.042 |
| 3. Attrition-milled with zircon | 0.047[a] | 0.036 |

[a] This figure is lower than the first two because of magnetite removed with zircon on tabling.

Flotation was not quite as efficient as magnetic separation for the removal of liberated iron-bearing particles.

## Cases of Small Benefit by Attrition Milling

With some rocks attrition milling has done little, if any, good; one example was an iron-stained feldspar from Warren, Maine. The crude rock occurred as pieces from 2 to 10 in. in size. The pieces were coated with an iron stain but showed little or no staining inside after being crushed. The rock was crushed past 20 mesh and froth-floated. The feed carried 0.16 per cent $Fe_2O_3$. The reagents used and the results of the separation were:

| Reagents | Rougher, Lb. per Ton | Products | Weight, Per Cent | $Fe_2O_3$, Per Cent |
|---|---|---|---|---|
| Oleic acid | 1.0 | Concentrate | 3.3 | |
| Napthenic acid sludge (S. Swabacher & Co.) | 1.0 | Tailing | 96.7 | 0.11 |
| $Na_2SiF_6$ | 0.8 | | | |

The oleic acid was emulsified in a 5 per cent solution in water of naphthenic acid sludge.

For attrition milling the minus 200-mesh fraction of the feed was removed. The plus 200-mesh fraction was treated for 20 min. at 67 per cent solids with minus 35 plus 65-mesh garnet amounting to 20 per cent of the weight of the feed. The garnet was tabled out of the attrition-mill product, which was recombined with the fines for flotation. Treatment with the above reagent combination gave the following results: concentrate, 3.5 per cent by weight; tailing, 96.5 per cent by weight containing 0.10 per cent $Fe_2O_3$. As relatively few particles were iron-stained, little was gained by attempting to remove the stain.

The flotation was carried out in a slightly acid circuit owing to the presence of the acid salt, sodium silicofluoride. The napthenic acid sludge is a sulphonated type of collector. The sulphonated and sulphated types of collector are most powerful in an acid circuit and most of them become detergents in an alkaline circuit. Oleic acid will film iron oxide minerals more easily in a slightly acid circuit, but frequently it is difficult to obtain frothing. The combination of oleic acid and napthenic acid sludge has proved satisfactory for the flotation of many high-iron minerals.

Sodium silicofluoride acts to make complex soluble aluminum, which prevents activation and flotation of the feldspar by the aluminum. When the silicofluoride was omitted 20 per cent of the feed went into the concentrate, as compared with 3.3 to 3.5 per cent when it was present. This deactivation by sodium silicofluoride of normally non-soap-floating silicates when activated by aluminum has been observed in slightly alkaline as well as in acid circuits.

Attrition milling did not improve flotation separation of an andalusite rock from Inyo County, California. The rock contained andalusite, quartz, corundum, and pyrophyllite. It was desired to obtain a concentrate of corundum and andalusite and to reject pyrophyllite and quartz.

Surface contamination of the minerals of this rock was as great or greater than that of any rock tested in this laboratory. When the rock was ground to pass 65 mesh and froth-floated with the usual combination of oleic acid and sodium silicate used for floating highly aluminous minerals, it showed no selectivity. Quartz was floated as easily as was andalusite or corundum, and if sufficient collector was used and the flotation continued long enough the entire charge was floated. The last to float was the coarser part of the feed. This is an example of the fact that the coarsest fraction of a "dirty" mineral is the most difficult to float. When the feed was attrition-milled some selectivity was noticed in the flotation, but the separation was still poor.

The only method that effected an acceptable separation with anionic collectors was the use of a hydrofluoric acid wash. The feed was treated for 5 min. with a 5 per cent solution of the acid, then the acid was drained and washed off, and the feed was froth-floated with the following reagents:

| Reagents | Pyrophyllite Rougher, Lb. per Ton | Andalusite Rougher, Lb. per Ton |
|---|---|---|
| Diamyl amine | 0.27 | |
| $H_2SO_4$ | | 2.0 |
| $Na_4P_2O_7$ | | 1.0 |
| $Na_2SiF_6$ | | 3.0 |
| Napthenic soap E (S. Swabacher & Co.) | | 3.0 |

Diamyl amine gave a better recovery of pyrophyllite than did pine oil. Tetrasodium pyrophosphate was used to complex any iron put into solution by the acid circuit, and sodium silicofluoride was used to complex aluminum. The results of this separation were:

| Products | Weight, Per Cent | Sink in $C_2H_2Br_4$, Per Cent |
|---|---|---|
| Pyrophyllite concentrate | 8.1 | 26.2 |
| Andalusite concentrate | 71.5 | 86.6 |
| Tailing | 20.4 | 17.1 |

Analysis was made by float-and-sink separation in acetylene tetrabromide (sp. gr., 2.9), as this method shows the distribution of high-alumina minerals. Pyrophyllite and quartz float in this liquid, whereas andalusite and corundum sink.

Substitution of attrition milling for the hydrofluoric acid wash gave much poorer results. The surface dirtiness of the minerals apparently was due to soluble aluminum rather than to pyrophyllite smearing. As a result, quartz and pyrophyllite could be floated from andalusite and corundum in an alkaline circuit with cationic collectors and suitable modifiers. The cationic collectors, unlike the anionic collectors, are not highly sensitive in a neutral or alkaline circuit to contamination by aluminum or iron. Quartz can be floated from highly aluminous minerals by DP-243 (laurylamine hydrochloride) in an alkaline circuit when modified with calgon (sodium hexametaphosphate) or tetrasodium pyrophosphate, or by cetyl trimethyl ammonium bromide when modified with tetrasodium pyrophosphate. The quartz and pyrophyllite of this rock were concentrated with the following reagent combination:

| Reagents | Rougher, Lb. per Ton | Cleaner, Lb. per Ton |
|---|---|---|
| NaOH | 1.0 | 1.0 |
| Calgon | 2.0 | 2.0 |
| DP-243 | 0.25 | 0.06 |
| Pine oil | 0.125 | 0.125 |

Results of this separation were:

| Products | Weight, Per Cent | Sink in $C_2H_2Br_4$, Per Cent |
|---|---|---|
| Cleaner concentrate | 24.5 | 16.4 |
| Middling | 4.1 | 63.5 |
| Tailing | 71.4 | 86.1 |

The grade and recovery of andalusite and corundum in the tailing product closely approximate those of the andalusite-corundum concentrate obtained in the preceding test, and the separation was obtained without the troublesome and expensive hydrofluoric acid wash.

Neither attrition milling nor washing with a cleaning chemical improved this separation greatly. The phosphate modifiers do not render aluminum silicates nonfloatable to the cationic collectors. They merely increase the quantity of collector required for their flotation without materially affecting the flotation of quartz. Because of this fact, it has been impossible to obtain much more complete separations than the one given. A similar separation has been obtained in the flotation of quartz from feldspar when the pulp was further modified by the addition of 4 to 8 lb. per ton of potassium chloride.

## Determining Optimum Attrition

Investigations to determine the most efficient conditions for the attrition grinding of sands have been conducted with the Jean (Nev.) sand. The effect of varying pulp density on Jean sand with no grinding medium, and a 5-min. grinding period is as follows:

| Solids, Per Cent | $Fe_2O_3$ in Nonmagnetic Sand, Per Cent | Solids, Per Cent | $Fe_2O_3$ in Nonmagnetic Sand, Per Cent |
|---|---|---|---|
| 25 | 0.061 | 67 | 0.055 |
| 50 | 0.054 | 75 | 0.066 |

The pulp density for maximum efficiency is 50 to 67 per cent solids.

The effect of the addition of a hard grinding medium to Jean sand at 67 per cent solids, 2½ min. of grinding and varying percentage of minus 48 plus 65-mesh zircon is as follows:

| Zircon, Per Cent | $Fe_2O_3$ in Nonmagnetic Sand, Per Cent | Zircon, Per Cent | $Fe_2O_3$ in Nonmagnetic Sand, Per Cent |
|---|---|---|---|
| 10 | 0.057 | 30 | 0.055 |
| 20 | 0.056 | 50 | 0.052 |

By the addition of 30 per cent of the weight of the feed of zircon, the same ferric oxide content is attained in 2½ min. as in 5 min. without the zircon.

To compare the effectiveness of various sizes of the grinding medium, tests were run with three sizes of zircon on Jean sand at 67 per cent solids, 2½ min. of attrition, and 20 per cent of zircon. The results were as follows:

| Size of Zircon, Mesh | $Fe_2O_3$ in Nonmagnetic Sand, Per Cent |
|---|---|
| −20 + 35 | 0.054 |
| −48 + 65 | 0.056 |
| −65 + 100 | 0.058 |

All the tests described were run with the stator having fins at an angle of 35° to the vertical. The blades sloped in the direction of rotation of the rotor from bottom to top. The impeller used had blades set at an angle of 45° to a tangent to the circular blade holder at the point of intersection of this circle by the blade. The rotor was rotated so that the blades "bit" into the slurry.

Rotor No. 2, with the blades making an angle of 30° to the tangent, was used in attrition-milling a sample of Jean (Nev.) sand. The sand was attrition-milled for 20 min. at 67 per cent solids with 20 per cent of its weight of minus 48 plus 65-mesh zircon. The nonmagnetic fraction, after removal of zircon, contained 0.048 per cent $Fe_2O_3$. Sand receiving the same treatment with rotor No. 1 contained 0.050 per cent $Fe_2O_3$. Stator No. 2, which was rubber-lined and had vertical fins, was used with impeller No. 1 to treat Jean (Nev.) sand under similar conditions. The sand product contained 0.041 per cent $Fe_2O_3$. To determine whether the increased efficiency was due to the rubber lining or the vertical position of the fins, stator No. 1 was lined with rubber, and sand was treated in it with rotor No. 1 under the above conditions. This product contained 0.044 per cent $Fe_2O_3$.

## SUMMARY

In studies of chemical and mechanical cleaning it has frequently been found that the surfaces of mineral particles that are ready for flotation, although apparently clean, have been polluted to such an extent that flotation is erratic and unreliable. While this result may not be new, it is important. Experimenters spend too much time seeking new flotation reagents that will give more selective filming, when actually their troubles are due rather to impurities that either mask the true mineral surface or act as activators on surfaces of minerals that are not to be floated.

Every mineral taken from the ground has a long history of solutions that have percolated over, around, or through it, and one must suspect every cleavage plane of having been penetrated and polluted. Purchase of "pure" minerals for synthesizing mixtures during flotation researches should not be assumed to guarantee the purity of a freshly cleaved surface. The ease with which sulphide mineral surfaces oxidize has been recognized, and means have been taken to remove oxidation films, but the contamination of surfaces is a more profound and ancient phenomenon. Minerals as mined are still saturated with the last solutions that circulated over them, and activating ions such as iron, aluminum, and silicate must be credited not only with having penetrated major and minor cracks but also with having diffused into the cleavage planes.

Using this philosophy as a basis, the authors investigated various nonmetallic minerals, regarding a nonselective separation merely as an indication that either chemical or mechanical "conditioning" or cleaning of surfaces exposed by grinding was the next necessary step. Only after such precautions could quartz always be made to behave like quartz.

This procedure has resulted in many new separations of minerals and an increase in the sharpness of selection in some otherwise imperfect separations. It is believed that by applying these simple principles an important step can be made in evolving the art of flotation into a more exact science.

## Acknowledgments

Acknowledgment is made to Dr. Alton Gabriel, associate chemist-petrographer, Eastern Experiment Station, Bureau of Mines, for his advice and optical studies of rocks and products; to Mr. Morris Slavin, assistant spectrographer, for spectrographic analyses of products; to Miss Mary Fletcher, junior scientific aide, for chemical analyses; and to Mr. R. C. Kudlich, superintendent, for assistance in design and construction of attrition mills.

# New Flotation Reagents*

By R. S. Dean,† Member A.I.M.E., and A. B. Hersberger‡

(New York Meeting, February, 1935)

Although it is obvious that in any flotation process we must have a froth, in recent years the development of collecting reagents has caused the possibilities of better frothing agents to be overlooked. Some investigators have even gone so far as to say that the number of satisfactory frothing agents was sufficient. A little consideration will show, however, that the reagents available in the past were far from ideal frothers. The properties of an ideal frother for flotation work may be set down as follows:

1. It must form in low concentrations a copious but not too persistent froth.
2. It must be insensitive to hydrogen-ion concentration of the pulp; that is, it must froth equally well in an acid or alkaline medium.
3. It must be insensitive to salts, even in high concentration.
4. It must be absolutely noncollecting to both sulfides and nonsulfides.
5. Its frothing properties must not be affected by collecting reagents, including soap, the most generally used nonsulfide collector.
6. It must readily emulsify and disperse any insoluble collecting agent that is likely to be used.

Clearly the existing frothers do not qualify. Pine oil, for example, is an acceptable frother for many purposes but if used in soap flotation a delicate balance between pine oil and soap must be struck because, as pointed out by Coghill[1], these two reagents are incompatible in certain concentrations. The objections to soap itself as a frother are obvious, and the cresols and their substitution products all have some collecting power and very little emulsifying power.

The mechanism of frothing in flotation was early explained on the basis of the Harkins-Langmuir theory of oriented molecules.[2] These investigators showed that if an organic compound having an unsymmetrical molecule (in which one end of the molecule contained water-avid groups) was placed at an air-water interface it would be oriented on the interface with the water-avid group toward the water, since a drop of such organic compound placed on water would spread to a layer one molecule thick, so that all the water-avid groups might be in contact with water. If the compound were water-soluble, it would still be adsorbed at the surface, with the water-repellent groups sticking out into air. It is clear that such reagents would tend to stabilize a froth or other system of greatly extended air-water interface.

---

* Printed by permission of the Director, U. S. Bureau of Mines. Manuscript received at office of Institute Nov. 13, 1934. Issued as T. P. 605, February, 1935.

† Chief Engineer, Metallurgical Division, U. S. Bureau of Mines, Washington, D. C.

‡ Chemistry Department, University of Maryland, College Park, Md.

[1] References are at the end of the paper.

Later investigators of flotation phenomena have accepted this explanation. Taggart, Taylor and Ince[3] summarize the requirements of a frothing reagent as follows:

> For this service (frothing, noncollecting) a reagent should contain an oxygen-bearing water-avid group. Preferably CH, COOH, CO, or COOR and preferably also one such group only. The amide group $CONH_2$ will serve as a water-avid group but appears in many instances to have a harmful effect on collecting. Attached to the oxygen-bearing group there should be a structure composed of carbon and hydrogen atoms containing preferably at least six carbon atoms that are not directly attached to the oxygen-bearing group. There must be an appreciable solubility but the solubility rating should preferably be slight; i.e., around 1000 mg. per liter, although many more soluble substances are satisfactory frothers.

In an earlier paragraph these authors conclude that the hydrocarbon chain must not be too long, since cetyl alcohol $CH_3(CH_2)_{14}OH$ is not soluble enough to be a frothing agent.

Starting from the same oriented-molecule theory of Harkins, Harris[4] has developed a line of reasoning somewhat different from that expressed above, and has produced a whole series of substances, which are in quite a different class from the heretofore available frothers, some of which closely approach the ideal frothing agent.

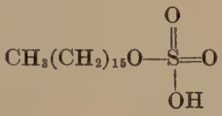
According to Harris, the problem of a frother must be solved by obtaining a proper balance between water-avid and water-repellent groups. He found, in agreement with Taggart, Taylor and Ince, that, if the water-avid group were a simple hydroxyl or carbonyl group, the substance became of no use above 6 or 8-carbon atoms owing to insolubility. If, however, these water-avid groups were properly chosen, substances with 16 or more carbon atoms could be used with startling results. To use a very crude analogy, if the water-avid tail were made heavy enough and active enough it pulled in the whole dog; hence the substance became soluble or at least readily dispersable in water. Thus cetyl alcohol, which we may write

$$CH_3 - (CH_2)_{14} - OH$$

is a nonfrother, while the following compounds with comparable carbon chains are the nearest approach we have found to ideal frothing agents for flotation:

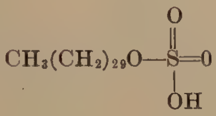
Cetyl ester of betaine hydrochloride

Cetyl hydrogen sulfate

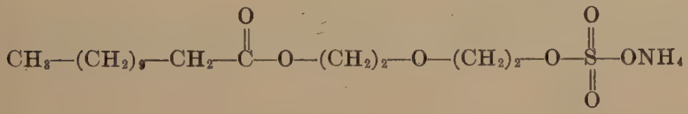


$CH_3(CH_2)_{15}O—\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{S}}=O$

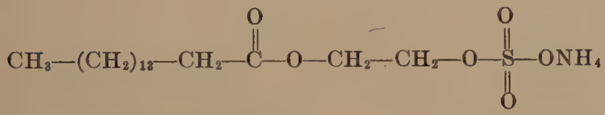
Melissyl hydrogen sulfate



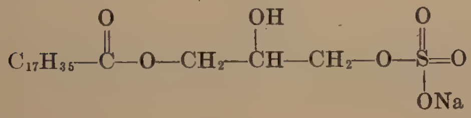
$CH_3(CH_2)_{29}O—\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{S}}=0$



$CH_3—(CH_2)_9—CH_2—\overset{\overset{O}{\|}}{C}—O—(CH_2)_2—O—(CH_2)_2—O—\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}—ONH_4$

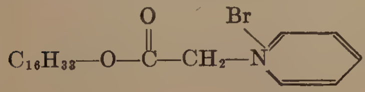


$CH_3—(CH_2)_{13}—CH_2—\overset{\overset{O}{\|}}{C}—O—CH_2—CH_2—O—\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}—ONH_4$

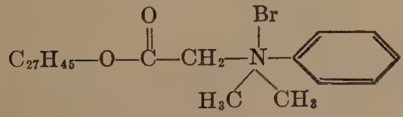


$C_{17}H_{35}—\overset{\overset{O}{\|}}{C}—O—CH_2—\overset{\overset{OH}{|}}{CH}—CH_2—O—\overset{\overset{O}{\|}}{\underset{\underset{ONa}{|}}{S}}=O$

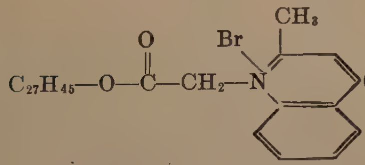
Potassium cetyl sulfate
Sodium cetyl phosphate
Melissyl ester of betaine hydrochloride



(Carbopalmitoxy) methyl pyridinium bromide



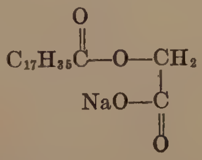
(Carbocholesteroxy) methyl dimethylphenylammonium bromide



(Carbocholesteroxy) methyl quinaldinium bromide

Cetyl ester of dimethylaminoacetic acid hydrobromide

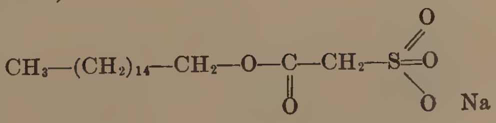
Stearyl glycollic acid, sodium salt



$C_{17}H_{35}\overset{\overset{O}{\|}}{C}—O—CH_2$
$NaO—\underset{\underset{O}{\|}}{C}$

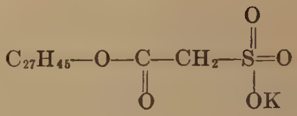
Monostearine sulfoacetate (sodium salt)

Cetyl sulfoacetate (sodium salt)



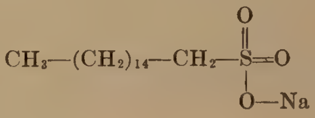
$CH_3—(CH_2)_{14}—CH_2—O—\underset{\underset{O}{\|}}{C}—CH_2—\overset{O}{S}=O \quad O \; Na$

Cholesteryl sulfoacetate (potassium salt)



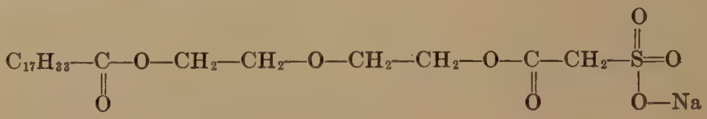
$C_{27}H_{45}-O-\underset{\underset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{\underset{\underset{OK}{|}}{S}}=O$

Cetyl sulfonic acid (sodium salt)



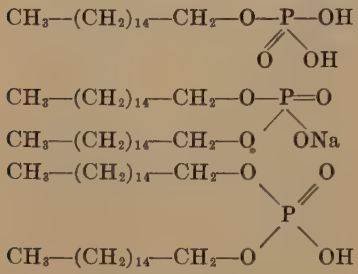
$CH_3-(CH_2)_{14}-CH_2-\overset{\overset{O}{\|}}{\underset{\underset{O-Na}{|}}{S}}=O$

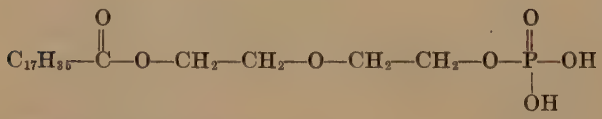
Oleyl diethyleneglycol sulfoacetate



$C_{17}H_{33}-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_2-O-CH_2-CH_2-O-\underset{\underset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{\underset{\underset{O-Na}{|}}{S}}=O$

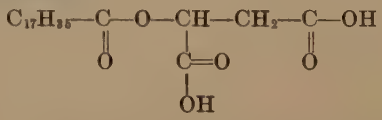
Stearyl diethyleneglycol sulfoacetate, sodium salt





$C_{17}H_{35}-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_2-O-CH_2-CH_2-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-OH$

Stearyl tartaric acid
Mucic acid monopalmitate
Stearyl malic acid,



$C_{17}H_{35}-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{\underset{OH}{|}}{\underset{C=O}{|}}}{CH}-CH_2-\underset{\underset{O}{\|}}{C}-OH$

## FLOTATION TESTS WITH NEW FROTHING AGENTS

Emulsol reagent, X-1, has been selected as typical of this group of reagents and has been used almost exclusively in testing work. This substance froths readily in amounts of 0.2 lb. per ton of ore, using a 20 per cent pulp, in either acid or alkaline condition. The froth is somewhat more watery than the usual flotation froth. Tests showed that the froth was absolutely barren when any of the common sulfide or nonsulfide minerals except graphite or talc were used at 65 mesh. By the use of oleic acid as a collector calcite, rhodochrosite, spatite and scheelite were readily floated. The reagent concentration was as follows: X-1, 0.25 lb. per ton ore; oleic acid, 0.25 lb. per ton ore; sulfuric acid, 0.1 lb. per ton pulp. By increase of acid concentration a point is reached where each of these minerals is depressed, as follows: rhodochrosite, 4 lb. per ton pulp; calcite, 3.0 lb. per ton pulp; scheelite, 0.6 lb. per ton pulp; apatite, 0.4 lb. per ton pulp.

Thus it will be seen that there is available a flotation process in which relatively high acid concentrations can be employed as a means of obtaining selectivity. As usual with flotation work, the results recorded above for pure minerals are at best only a qualitative guide in working with actual ores, probably because of coatings. Additional tests showed that sodium carbonate and sodium silicate were without effect on the frothing qualities of the reagent, and it could be used satisfactorily even in saturated brine.

## TESTS ON ACTUAL ORES

The use of the reagent in testing on actual ores is illustrated by the following examples.

*Concentration of a Kyanite Ore.*—The ore consisted of kyanite, quartz, limonite, rutile, garnet and clay. The material was ground through 40 mesh and the kyanite separated from quartz in a slightly acid circuit by the use of 0.2 lb. per ton X-1 and 0.02 lb. per ton oleic acid. This concentrate was contaminated with iron minerals. The flotation of the iron minerals was inhibited by ball milling with 2.0 lb. sulfuric acid per ton and a little X-1. The results of a single flotation after such conditioning are given in Table 1. A Fahrenwald subaeration machine was used.

TABLE 1.—*Concentration of Kyanite Ore*

| | Per Cent Weight | Assay, Per Cent | | | Sp. Gr. |
|---|---|---|---|---|---|
| | | $Al_2O_3$ | $Fe_2O_3$ | Quartz | |
| Concentrates...... | 14.8 | 60.51 | 0.49 | 0.62 | 3.52 |
| Middlings......... | 16.6 | | | | |
| Tailings.......... | 68.5 | 3.79 | | | 2.65 |

*Flotation of Graphite Ore.*—The ore as received will pass a 40-mesh screen and is fine enough to float. It consists chiefly of graphite and silica sand. The graphite particles are associated very closely with the gangue and very fine grinding is required to liberate them.

A high-grade concentrate is desired, with the particle size as large as possible, since large-flake graphite is of considerably more value than fine graphite.

The ore contains considerable clay, which was removed by desliming before flotation.

Preliminary tests showed that the graphite was readily floated, using a very small quantity of X-1 and oleic acid and 0.2 lb. per ton of sulfuric acid.

Concentrates obtained after using one cleaner operation contained 68 per cent carbon. Further cleaner operations failed to increase the percentage of carbon, but ball milling the concentrates for about 15 minutes and refloating gave considerably better concentrates. Concentrates containing 82.3 per cent carbon could be obtained easily. Ball milling for a longer period and then floating gave a concentrate analyzing 83.5 per cent carbon.

Typical results obtained by operations on deslimed ore are given in Table 2. The middlings contained more graphite than the feed and can be re-treated. The recommended flow sheet is as follows:

TABLE 2.—*Typical Results on Desliming Graphite Ore*

| | Weight, Per Cent | Carbon, Per Cent |
|---|---|---|
| Concentrate | 2.25 | 83.5 |
| Middlings | 7.10 | |
| Tails | 90.65 | virtually none |

SCREEN ANALYSIS OF PRODUCT

| | PER CENT |
|---|---|
| Retained on a 60-mesh screen | 12.2 |
| Retained on a 80-mesh screen | 28.8 |
| Retained on a 100-mesh screen | 27.0 |
| Retained on a 200-mesh screen | 24.7 |
| Pass 200-mesh screen | 8.3 |

Ore
↓
Grind to pass 40 mesh
↓
Deslime
↓

| | |
|---|---|
| Float using | Tails |
| 0.5 lb. per ton $H_2SO_4$ | and 0.1 lb. per ton X-1, 0.01 lb. oleic acid |
| Cleaner No. 1 | Tails back |
| 0.2 lb. per ton $H_2SO_4$ | 0.1 lb. per ton sodium silicate and 0.05 lb. per ton X-1, and 0.005 oleic acid |
| Ball mill | |
| Cleaner No. 2 | Tails back |
| 0.2 lb. per ton $H_2SO_4$ | 0.1 lb. per ton sodium silicate and 0.05 lb. per ton X-1, and 0.0005 lb. per ton oleic acid |
| Concentrate | |
| 83.5 per cent carbon. | |

*Flotation of a Barite Ore.*—The ore contained barite, calcite, fluorite and quartz. The barite is readily floated from the 100-mesh ore by the use of 0.2 lb. per ton X-1 and 0.02 lb. per ton oleic acid after conditioning with 0.2 lb. per ton sulfuric acid and 1 lb. per ton sodium silicate. The resulting product analyzed 98.5 per cent $BaSO_4$, with a recovery of 93.2 per cent.

*Flotation of Iron Ores.*—The separation of hematite from quartz has never been very satisfactory in ordinary soap flotation because of the activation of quartz by the iron salts. The use of the present reagents as frothers permits operation in a more acid circuit and it has been found that 0.2 lb. per ton of acid is enough to inhibit quartz flotation when oleic acid is used as collector. The froth is not well suited, however, to carrying large amounts of fairly coarse material, and we prefer to use smaller amounts of soluble oils as collectors, which is made possible by the emulsifying power of reagents like X-1. In this way quantitative separation of synthetic mixtures of quartz and hematite may be made. The degree of separation in actual ores is determined by the extent to which coating of the quartz by fine iron-oxide particles can be prevented. The advantage of explosion shattering as a method of ore preparation is indicated.

*Flotation of Sulfide Ores.*—The flotation of sulfides can be effected by the use of xanthates or other sulfide-collecting agents. The use of X-1 as a frother is particularly advantageous where sulfide and non-sulfide minerals are to be floated consecutively. By the use of an alkaline circuit (1 lb. soda ash per ton) sulfides may be depressed and the non-sulfides floated with oleic acid, or the sulfides can be first floated with xanthate.

*Flotation of Phosphate Rock.*—The separation of phosphate from quartz by flotation is readily accomplished by the use of the following reagent combination: 0.5 lb. per ton X-1, 0.2 lb. per ton soda ash, 1 lb. per ton sodium silicate, 1 lb. per ton oleic acid. No satisfactory separation can be made in an acid circuit.

*Flotation of a Chromite Ore.*—In a chromite ore containing olivine as gangue, a concentrate containing 58 per cent $Cr_2O_3$ was made by floating the olivine with X-1 and oleic acid in a circuit containing 0.2 lb. per ton sulfuric acid.

It is not necessary to cite further examples, since it is obvious that virtually all minerals that have been floated can be treated using the new reagent as frother. The advantages, if any, over other frothers will depend on the separations to be made.

## NEW COLLECTORS

So far we have concerned ourselves entirely with previously known and used collectors. The properties of X-1 permit use of collectors not heretofore possible; for example, the insoluble paraffin oils. The selectivity of the paraffin oils was the basis of many processes developed immediately preceding froth flotation. Among such processes, depending on the selective action of oils, may be mentioned the Murex process, in which magnetite was selectively attached to galena and the agglomeration and tabling process of Cattermole. The use of X-1 as an emulsifier greatly facilitates these old processes and allows them to be carried out in acid, alkaline and brine circuits. These improvements greatly increase the scope of these processes. Furthermore, the great emulsifying power of X-1 permits the use of these insoluble oils as selective collectors in froth-flotation processes also. A very large field of possible new collectors is opened up thereby.

Another group of new collectors has been made possible by the use of X-1 as a frother. Oleic acid is the most generally useful collector for nonsulfides, having been used by Thornberry as long ago as 1916 in an attempt to float copper carbonate.[5] The mechanism of collection by oleic acid is not fully understood, but it must be related in some way to the structure of the oleic acid molecule. There are several ways in which this may be modified. For example, the oleic acid may be sulfonated. This sulfonated oleic acid is a much less universal collector than oleic acid. By further modification to form the butyl ester of sulfonated oleic acid, a substance with only very slight collecting properties is obtained. Thus a series of compounds decreasing in collecting ability may be made, starting with oleic acid and modifying it in various ways.

As an example of the use of sulfonated oleic acid as a collector may be mentioned the separation of limestone from pyrolusite. In this instance the calcite may be floated by the use of a slightly acid circuit with X-1 and sulfonated oleic acid.

We have attempted to show in this paper the new possibilities in flotation made possible by the development of highly efficient frothers and emulsifiers. Flotation investigators will realize that no set of rules may be set up that will enable a flow sheet to be specified for an ore without experimentation. The authors believe, however, that the use of the new reagents greatly simplifies the problem of establishing selective flotation conditions.

## ACKNOWLEDGMENT

The assistance of Mr. B. R. Harris, of the Emulsol Corporation, in furnishing the reagents employed and making many suggestions throughout the work is gratefully acknowledged.

## REFERENCES

[1] W. H. Coghill and J. B. Clemmer: Soap Flotation of Nonsulfides. *Trans.* A.I.M.E. (1934) **112**, 449.

[2] R. S. Dean: The Theory of Flotation. *Min. & Sci. Pr.* (1921) **122**, 291.

[3] A. F. Taggart, T. C. Taylor and C. R. Ince: Experiments with Flotation Reagents. *Trans.* A.I.M.E. (1930) **87**, 319.

[4] U.S. Patents 1917249, 1917240, 1917251, 1917252, 1917253, 1917256, 1917257, 1917258, 1917259, 1917260, and other patents pending.

[5] H. H. Thornberry: *Bull.* Univ. of Missouri School of Mines and Metallurgy (1916) **3**, No. 1, 38.

# Froth Flotation of Fluorspar

By David R. Mitchell* and Henry Emmett Gross,† Members A.I.M.E., and
H. E. Oehler,‡ Student Associate A.I.M.E.

(New York Meeting, February, 1938)

The production of fluorspar is one of the smaller nonmetallic industries in the United States with a capital investment—about \$10,000,000. Shipments from United States mines[1] in 1936 totaled 176,231 short tons valued at \$3,111,268, an average price of \$17.65 per ton. The United States produces about 40 per cent of the world's fluorspar, of which about 90 per cent comes from the Illinois and Kentucky deposits along the Ohio River.[2] Further detailed information on the fluorspar industry in the United States is given by Hatmaker and Davis.[28]

Fluorspar is marketed according to the following relative quantities and specifications:

| Use | Form | Consumption in 1936, Per Cent | Specifications, Per Cent | | |
|---|---|---|---|---|---|
| | | | $CaF_2$ | $SiO_2$ | $Fe_2O_3$ |
| Metallurgical | Gravel or lump | 79 | +85 | −5 | |
| Ceramic | Ground | 10 | +95 | −3 | −0.1 |
| Acid | Ground | 11 | +98 | −1 | |

The concentration of the coarser sizes presents relatively little difficulty, good recoveries being obtained with jigs and tables. However, sizes smaller than about 10 mesh cannot be successfully treated by ordinary gravity separation methods and so have been accumulating as

---

The experimental data reported herein were obtained in the Mining Laboratories of the University of Illinois; most of the experimental work was done by H. E. Gross while a Research Graduate Assistant in the Engineering Experiment Station and presented as a thesis in partial fulfillment of the requirements for the degree of Master of Science in 1932. Manuscript received at the office of the Institute Jan. 15; revised June 13, 1938. Issued as T. P. 999 in Mining Technology, November, 1938.

* Professor of Mining Engineering, The Pennsylvania State College; formerly Associate Professor of Mining and Metallurgical Engineering, University of Illinois.

† Associate Professor of Petroleum Engineering, Agricultural and Mechanical College of Texas, College Station, Texas.

‡ Tau Beta Pi Fellow, University of Illinois, Urbana, Ill. Became a Junior Member of the Institute in September 1938.

[1] References are at the end of the paper.

waste containing a large percentage of fluorspar. In recent years attempts have been made to utilize froth flotation methods to recover the fluorspar in the tailings from jig and table mills.

The froth flotation separation of fluorspar from quartz has been worked out fairly satisfactorily; according to Medenbach[3] there are now three plants in Germany treating ores in which the gangue is chiefly quartz. When, however, the gangue contains considerable calcite, as in the Kentucky and Illinois deposits, the problem is more difficult. To the authors' knowledge, only one flotation plant is in operation in the Kentucky-Illinois district. A flowsheet of this plant has been published recently[4] but operating details are only briefly described.

Relatively little authoritative information has been published regarding the froth flotation of fluorspar from gangue containing calcite, and from time to time requests have been received at the University of Illinois for methods of treatment of ore of this type, particularly the immense tailing dumps that have been accumulating at plants in the Kentucky-Illinois district. In response to these requests studies were begun in the fall of 1931 and have been continued intermittently since then. The object of the investigations reported herein was to determine some of the fundamental froth flotation properties of fluorspar and associated gangue minerals, quartz and calcite, with the idea that the information so obtained might have some future commercial application. This paper is in the nature of a progress report and is incomplete in many respects.

The following items were studied in detail: (1) the character of the waste material from a fluorspar mill, especially as to mineral and particle size; and (2) the amenability of fluorite and gangue minerals to separation by froth flotation, as affected by (*a*) temperature variations in the flotation cell, (*b*) varying amounts of reagents, (*c*) pH and (*d*) size of mineral particles.

## WORK OF OTHER INVESTIGATORS

The earliest published information on the flotation of fluorspar known to the writers was reported by Richards and Locke[5] in 1925. They describe a plant at Trail, B. C. Flotation was carried out with oleic acid and soda ash at 80° C. in Callow cells. The feed assayed 66 per cent $CaF_2$ and the concentrate 92 per cent $CaF_2$ and 3 per cent $SiO_2$. It is not known whether this plant is still operating.

Prof. A. F. Taggart, of Columbia University, reported the flotation separation of calcite and fluorite from quartz in 1927.[6] In a private communication he stated that this work had been carried out in his laboratory several years prior to the publication. Reagents used were oleic acid and sodium silicate.

In 1928 Coghill and Greeman[7] reported an 81.1 per cent yield by flotation with oleic acid, sodium oleate, pine oil, soda and sodium silicate. Feed assaying 69 per cent $CaF_2$ and 27 per cent $SiO_2$ was concentrated in a single step to 98 per cent $CaF_2$.

Madel and Fischer[8] obtained, by application of oleic acid, oleate and xanthate, a concentrate of 99 per cent $CaF_2$ from ore analyzing 84.5 per cent $CaF_2$ and 13.7 per cent $SiO_2$. The yield in a single step was 75 per cent.

In U. S. Patent 1785992, Greeman and Williams[9] claim that the elimination of slime material is necessary for satisfactory separation from calcite. It is suggested that this be done by a desliming phase of froth flotation, using copper sulphate, phosphocresylic acid, and sodium sulphide, or by repeated agitation, settling and decantation. An excellent fluorspar concentrate could then be made using oleic acid, cresylic acid, and proper modifying reagents.

Cooper Shapley,[10] in U. S. Patent 1689693, claims to have produced a fluorspar concentrate by the use of soap from a highly siliceous ore mined in New Mexico.

Coghill and Clemmer[11] recommend elevated temperatures and state that for selective soap flotation the amount of soap rarely exceeds 100 to 150 parts per million of water.

Gaudin[12] says that while separation of fluorite from quartz is not difficult, the separation from calcite had not been accomplished practically up to the time of his publication (1932). He reports the laboratory separation of fluorite from calcite by treatment with hot copper sulphate, followed by flotation of the activated calcite with amyl xanthate. Consumption of reagents was large. Gaudin also discusses the effect of pH and the depression of calcite with colloidal hydroxides.

Greeman and Lilly,[13] in U. S. Patent 1926045, recommend the addition of oxidizing agents to the water or pulp prior to the frothing operation, whereby the fluorspar yield is increased. The favorable pH of the water is given as 7.

In 1934 J. M. Patek[14,15] discussed the use of colloidal depressing agents in soap flotation. He reported the flotation of fluorite from calcite by the use of 1½ lb. of tannic acid per ton of ore. The calcite probably became coated with colloidal tannic acid.

In the same year O'Meara and Clemmer[16] reported the flotation of fluorite from siliceous and calcareous gangue with sodium silicate, oleic acid, and an acid reagent. Concentrates of acid grade were obtained with recoveries of from 82 to 85 per cent.

The difficult problem of fluorite-calcite separation was studied by Moser[17] in Germany. He obtained a concentrate of 88.7 per cent $CaF_2$ from an ore of 20 per cent $CaF_2$ and 80 per cent $CaCO_3$ using chromic nitrate as a calcite depressant and sodium oleate as a collector for the fluorite. Sodium silicate also was used, and the best pH was found to be around 7.4. He also tried a sulphonated fatty alcohol as a collector, but the results were not satisfactory.

Ralston[26] abstracted work reported on by Eigeles[24,25] in Russia in which testing begun in 1929 has been carried to commercial practice. Oleic acid and a pH of 9.7 to 10.5 are used to get a plus 98 per cent fluorite concentrate. Ralston also states that Sinclair[27] reports that a small froth flotation plant was being installed near Ottoshoop, Zeerust district, western Transvaal, to produce acid-grade spar.

## THEORETICAL AND TECHNICAL ASPECTS OF THE FROTH FLOTATION OF FLUORSPAR

The froth flotation of polar nonmetallic minerals is accomplished primarily through the formation of insoluble soaps at the mineral surface. This may occur by reaction between dissolved soaps or fatty acids and either the mineral surface itself or ions or molecules of an activating agent adsorbed at the surface. Since soaps possess good frothing qualities, they may act as frothing agents as well as collectors. In fact, often the frothing action must be suppressed. Coghill and Clemmer state that the addition of five parts of pine oil per million of water is often necessary to impart enough brittleness to the froth to bring about the required selectivity. The pine oil probably affects the degree of flocculation.

The fatty acids that have been used most extensively in practice are oleic and palmitic, although others have been used in the laboratory.[12] Sulphonated fatty alcohols have been used in the separation of barite from calcite;[19,20] Moser, however, as mentioned before, found that in the flotation of fluorite from calcite better results were obtained with sodium oleate.

The depression of gangue minerals may be brought about by several methods. Most siliceous minerals are deflocculated by silicate solutions, the action on quartz being permanent. According to Vail[18] the dispersing power of silicates is improved with increased silica content, and silicates of compositions $Na_2O,2SiO_2$ and $Na_2O,3SiO_2$ seem to be preferred. The presence of soluble silicates hinders the precipitation of calcium soap from hard water and so promotes the formation and stabilization of lathers.

Sodium carbonate and sodium phosphate also have an inhibiting action on the flotation of quartz. Gaudin states that their action cannot be ascribed to their influence on the pH, since if the pH is adjusted to the same values with sodium hydroxide, the same effects do not necessarily obtain. He relates the effects to the properties of the anions: $CO_3^{--}$, $HCO_3^-$, and $HPO_4^{--}$.

The selective depression of calcite in the presence of fluorite is complicated by the fact that both minerals contain the same cation. However, according to Gaudin, separation may be accomplished by the use of certain salts, which form colloidal hydroxides. Moser found that when a mixture of fluorite and calcite was treated with chromic nitrate, a gray-green coating formed on the calcite, while the fluorite was unchanged in appearance. Possibly this may be explained on the basis of the difference in anions of the two minerals. Chromic fluoride is somewhat soluble, while the colloidal mixture of chromic hydroxide and carbonates, which would tend to form on the calcite surface, would be difficultly soluble, and would provide a gelatinous coating aiding dispersion.

Metal silicate gels have been used to depress calcite. According to Patek,[14] when a heavy metal salt and sodium silicate are added to an ore pulp a metal silicate gel is formed, which probably becomes adsorbed at the calcite surface because of a tendency toward chemical interchange. The use of an acid reagent with sodium silicate, as was done by O'Meara and Clemmer,[16] may have had the effect of increasing jellying and calcite solubility, resulting in the formation of a calcium silicate gel on the calcite.

## EXPERIMENTS AT UNIVERSITY OF ILLINOIS

The ore used in these tests was a table tailing from the Illinois-Kentucky fluorspar district, which assayed 47 per cent $CaF_2$, 31 per cent $CaCO_3$, and 22 per cent $SiO_2$. The samples used in the tests were relatively free of slimes.

A sizing test was made on the ore as received, and the sized products between consecutive meshes were analyzed. At first the analyses were made by precise quantitative methods, but as this practice was very slow, methods using heavy liquids for rapid mineral separation were tried.[21–23] Acetylene tetrabromide was found satisfactory for this purpose, since its specific gravity (2.97) is midway between that of fluorite (3.01–3.25) and those of the gangue minerals (calcite 2.71 and quartz 2.66). The sample to be tested was shaken with the acetylene tetrabromide and allowed to stand in a separatory funnel. The float-and-sink fractions were then drawn off and washed with benzene. Of the diverse sink fractions throughout the sieve range, only the minus 200-mesh material analyzed over 1 per cent $CaCO_3$. It tested 2.73 per cent $CaCO_3$, probably because of entrapment and difficulty in separating the very small sizes. This indicated that the fluorite was freed and the acetylene tetrabromide sink fractions were considered to be pure $CaF_2$. An askarite train was used to determine the $CaCO_3$ content of the float fractions, and $SiO_2$ was obtained by difference.

Fig. 1 depicts the character of the ore used in these tests. Fig. 1*a* indicates the weight per cent and analysis of each fraction passing through any sieve of size shown but retained on the next smaller size. The curves in Fig. 1*b* indicate similar data for the entire portion passing through any sieve.

The flotation tests were made in a 2000-gram laboratory-size Ruth subaeration machine. Since it was found necessary to heat the pulp, six Bunsen burners were mounted around the flotation cell for this purpose. Later a ½-in. steam line was placed in the impeller compartment, which proved satisfactory.

The customary test procedure was to put 5 liters of water in the cell and heat to the desired temperature. Water glass and sodium carbonate were then added, and the machine was charged with ore. At first 280-gram charges of ore were used in the trial runs, but later 2000-gram charges were adopted as standard procedure. When the pulp was thoroughly mixed a drop of oleic acid was added and the resulting froth was removed. This operation was then repeated, the skim from each successive drop going to an individual receptacle until no more mineral was floated. The various fractions were oven-dried at 110° C. and then weighed and set aside for analysis.

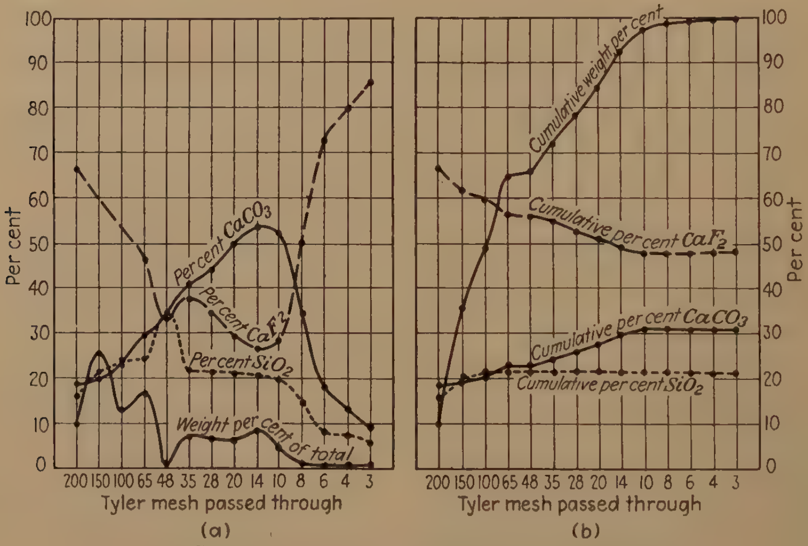


FIG. 1.—SIEVE ANALYSIS OF ORE USED IN FLOTATION TESTS.

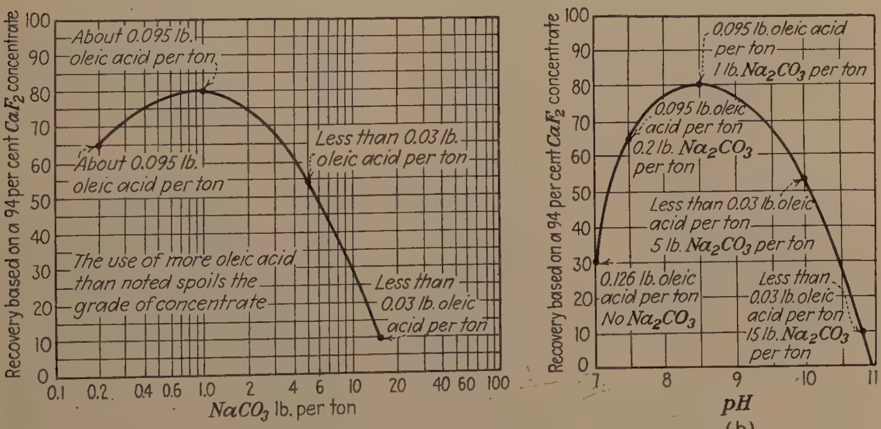
In converting the number of drops of oleic acid to pounds per ton of ore, the median of two types of progression was used. The first progression was based on the weight of the initial charge of ore, and the second was calculated by allowing for the amount skimmed off before the addition of each successive drop. Table 1 shows how this was done.

A series of preliminary runs indicated that the optimum cell temperature was approximately 60° C. A mineral-bearing froth did not form at lower temperatures. Good results were obtained from 60° to 90° C., but above 90° C. too much gangue was carried over. For economical reasons it would be advisable to use the lowest temperature consistent with good recovery.

TABLE 1.—*Progression in Converting Number of Drops of Acid to Pounds per Ton Ore*

| Number of Drops | Lb. per Ton Based on Initial Charge | Lb. per Ton Previous Skimming Deducted | Lb. per Ton Mean |
|---|---|---|---|
| 1 | 0.13 | 0.13 | 0.13 |
| 2 | 0.26 | 0.29 | 0.28 |
| 3 | 0.39 | 0.53 | 0.46 |
| 4 | 0.51 | 0.81 | 0.66 |
| 5 | 0.64 | 1.14 | 0.89 |
| 6 | 0.77 | 1.50 | 1.13 |
| 7 | 0.90 | 1.90 | 1.40 |
| 8 | 1.03 | 2.32 | 1.67 |
| 9 | 1.16 | 2.76 | 1.96 |
| 10 | 1.29 | 3.25 | 2.27 |

Another series of tests was made in which the amounts of water glass used were varied from 0.03 to 0.48 lb. per ton. The best fluorite recoveries were obtained using about 0.12 lb. of water glass of 1.40 sp. gr. per ton of ore. The tests were made on minus 48-mesh ore; the only other reagent used was oleic acid. The effect of the water glass would probably be changed somewhat by the presence of other reagents, but time was not available to investigate further in that direction; nor was there time to study the effects of other gangue depressants, such as chromic nitrate.

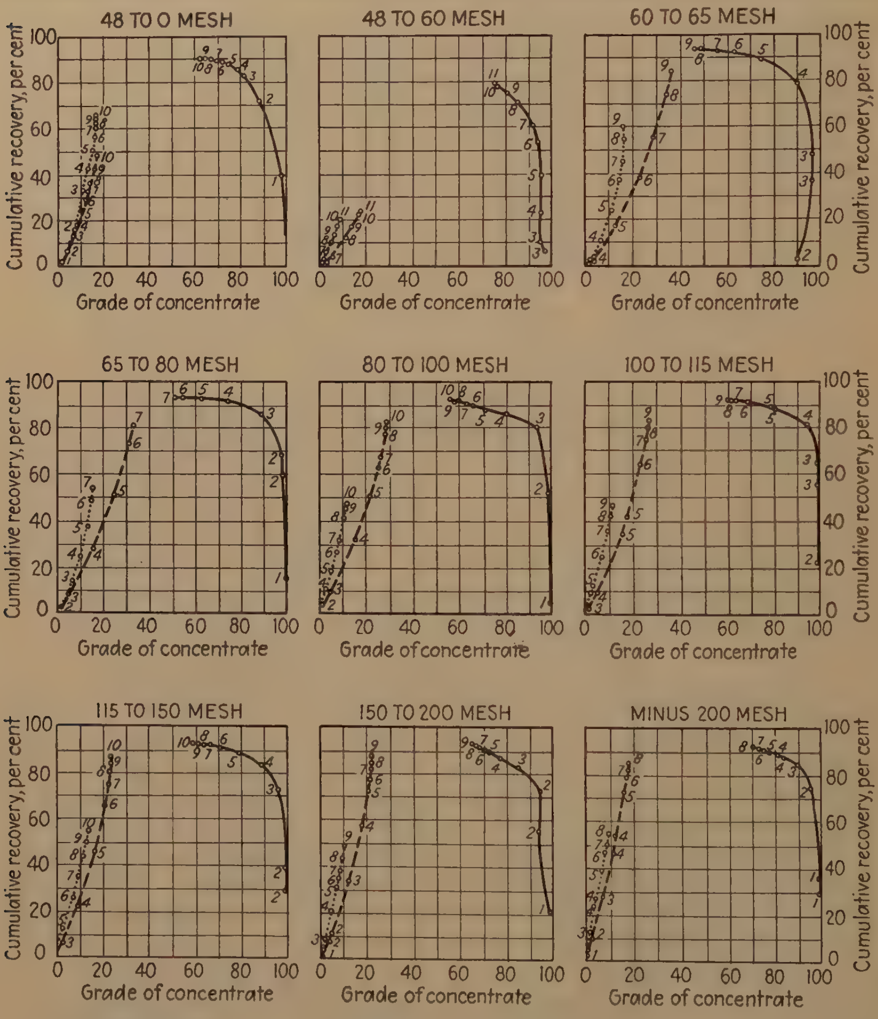


(a) (b)

FIG. 2.—RECOVERY VERSUS AMOUNT OF ALKALI USED AND pH IN FLOTATION TEST ON 48-MESH TO 0 MATERIAL.

Runs were made at 60° C. and 0.126 lb. of 1.40 sp. gr. water glass per ton was used.

Sodium carbonate was used for its inhibiting effect on the flotation of quartz and to regulate the pH of the pulp. Tests were made on minus 48-mesh material to determine the optimum amount, and Fig. 2 gives the results obtained. The recoveries plotted were based on a concentrate of 94 per cent fluorite. The amounts of oleic acid required are shown at each point; the use of more than these amounts lowered the grade of the concentrates. The optimum amount of sodium carbonate is about one pound per ton of ore; the best pH is 8.5. The pH was determined colorimetrically and with a glass electrode.

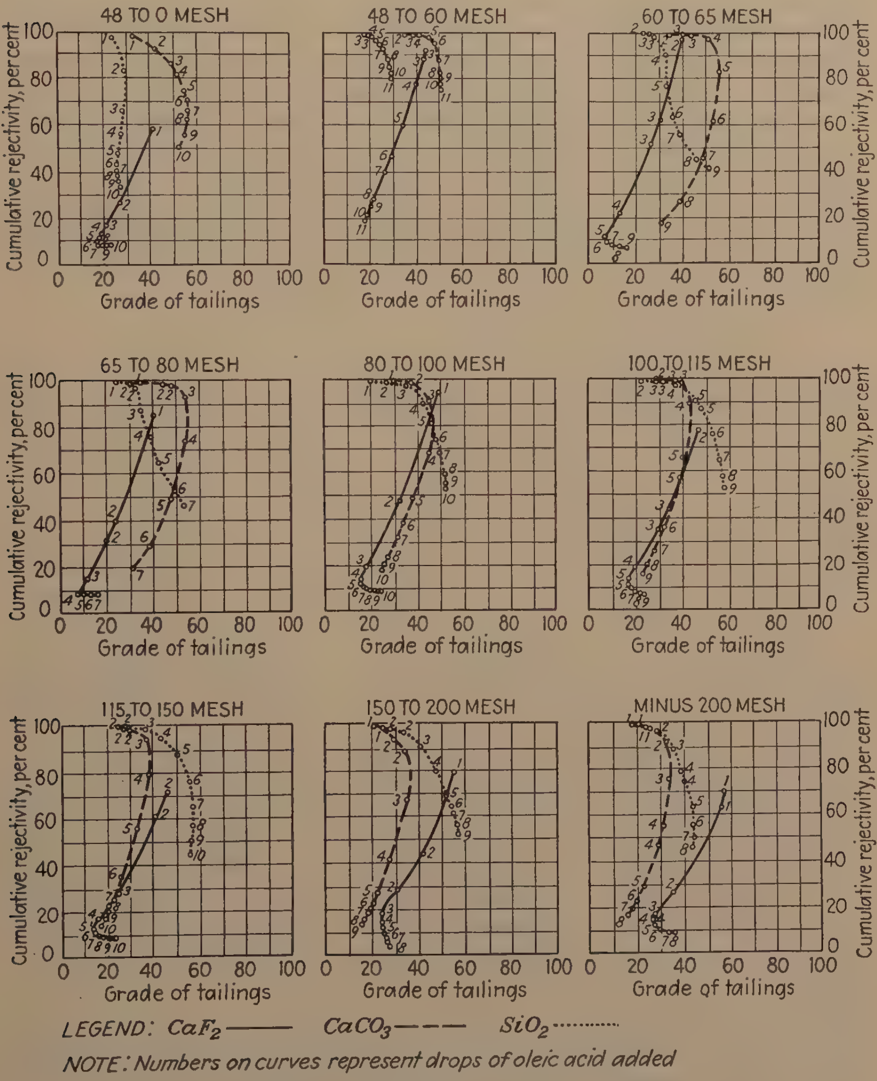


LEGEND: $CaF_2$ ——— $CaCO_3$ – – – – $SiO_2$ ··········

NOTE: Numbers on curves represent drops of oleic acid added

FIG. 3.—CUMULATIVE RECOVERY CURVES ON SIZED ORE.

Tests conducted with distilled water as well as with tap water failed to indicate any difference in results obtained. Stearic acid was used in one run and seemed to be just as good a collector as oleic acid.



LEGEND: $CaF_2$ ——— $CaCO_3$ – – – $SiO_2$ ··········

NOTE: Numbers on curves represent drops of oleic acid added

FIG. 4.—CUMULATIVE REJECTIVITY CURVES ON SIZED ORE.

The relative floatabilities of the various sizes of mineral particles were investigated by conducting a separate run on each of eight closely sized samples. One pound of sodium carbonate and 0.12 lb. of water slass (sp. gr. 1.40) were used per ton of ore in all tests, and the temperature was held at 60° C. The results are shown in Figs. 3 and 4, together with data from a test on 48-mesh to 0 material for comparison. In Fig. 3 the recoveries of each mineral are plotted against the grades of concentrate obtained for each drop of oleic acid added. The rejectivities are plotted similarly in Fig. 4.

To illustrate the meaning of these curves, consider those for the 48-mesh to 0 sample. Suppose that a product is wanted containing a minimum of 85 per cent fluorite and a maximum of 7 per cent silica. The cumulative recovery curve for fluorite indicates that about 2½ drops of oleic acid gives a concentrate containing 85 per cent $CaF_2$, but the silica-recovery curve indicates the maximum amount of collector to be 2 drops. More than this will increase the $SiO_2$ content of the froth above 7 per cent. The analyses of the concentrate and tailing, using 2 drops of oleic acid, would be as shown in Table 2.

TABLE 2.—*Analyses Using Two Drops Oleic Acid*

| Concentrate | | | Tailings | | |
|---|---|---|---|---|---|
| Assay | | Per Cent Recovery | Assay | | Per Cent Rejectivity |
| $CaF_2$ | 89 | 73 | $CaF_2$ | 27 | 27 |
| $CaCO_3$ | 4 | 7 | $CaCO_3$ | 44 | 93 |
| $SiO_2$ | 7 | 16 | $SiO_2$ | 29 | 84 |

Further treatment of the tailing to give the lowest grade of rejected material, as shown by the $CaF_2$ rejectivity curve, would require 4 additional drops of oleic acid. The middling and final tailing would then analyze as shown in Table 3.

TABLE 3.—*Analyses Using Four Additional Drops Oleic Acid on Tailings*

| Middling | | | Tailing | | |
|---|---|---|---|---|---|
| Assay | | Per Cent Recovery | Assay | | Per Cent Rejectivity |
| $CaF_2$ | 40 | 17 | $CaF_2$ | 17 | 10 |
| $CaCO_3$ | 25 | 22 | $CaCO_3$ | 57 | 71 |
| $SiO_2$ | 35 | 41 | $SiO_2$ | 26 | 43 |

In this manner product grades may be determined for any given set of conditions. It is interesting to note that the $CaF_2$ recovery curves for the finer sizes break off more sharply at the tops than do those for the coarser sizes and for the 48-mesh to 0 material.

Fluorite in the sizes coarser than 65 mesh was not readily floatable; sizes smaller than 65 mesh float readily, with recoveries from 72 to 80 per cent.

During the test on 48-mesh to 0 material, the froth skimmed off after each addition of oleic acid was subjected to a sieve analysis and then was analyzed for fluorite and gangue. Fig. 5 shows the cumulative recoveries obtained for each size, and it would seem from this that the finer the fluorite particles the more readily can they be recovered. The curves for the gangue minerals do not show such perfect regularity. However, it is readily seen that for satisfactory concentration of the ore tested the mineral particles should be ground smaller than 65 mesh.

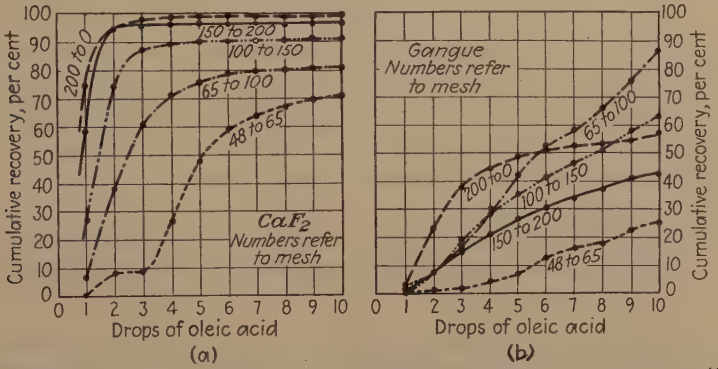


FIG. 5.—RECOVERY OF FLUORITE AND GANGUE MINERALS IN FROTH WITH 48-MESH TO 0 MATERIAL.

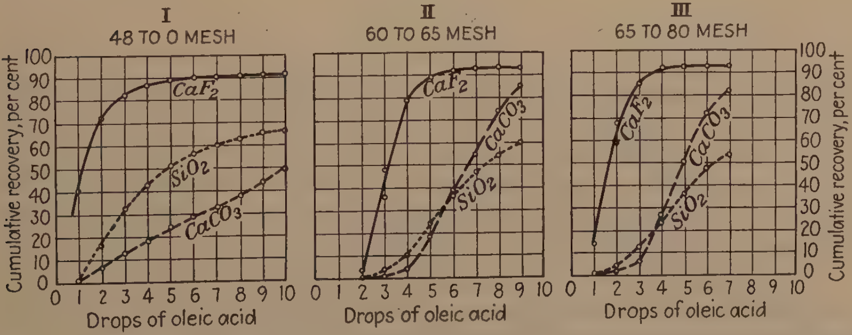


FIG. 6.—CUMULATIVE RECOVERY CURVES FROM FLOTATION STUDY OF SIZED ORE.

Fig. 3 shows that, for each drop of oleic acid added, in the 48-mesh to 0 size the silica was recovered at a higher rate than was the calcite. This was true for the more closely sized samples, however, only up to a certain point, after which the recovery of calcite exceeded that for the silica. Fig. 6 shows three sets of recovery curves plotted so as to better show this. The curves for the other closely sized samples are similar to those shown.

The highest selectivity indices are obtained with sizes ranging from 65 to 150 mesh.

## SUMMARY

A sample of table tailings from a fluorspar mill, containing a high percentage of calcite, was analyzed for particle size and mineral content. The minus 48-mesh portion was then used to study some of the froth flotation properties of fluorite and associated gangue minerals, quartz and calcite.

The best concentrates and the highest recoveries were obtained with cell temperatures of from 60° to 90° C.

The amount of reagents and the pH of the ore pulp were found to have pronounced effects on the recoveries obtained. About one pound of sodium carbonate per ton of ore proved to be the optimum amount. The best pH was 8.5. Water glass of 1.40 sp. gr. was used to the extent of 0.12 lb. per ton of ore. The consumption of fatty acid depended somewhat upon the amounts of other reagents used; too much fatty acid lowered the grade of concentrate.

Tap water proved to be fully as satisfactory as distilled water in these tests. Stearic acid was used as a collector in one run and gave results similar to those obtained with oleic acid.

Generally speaking, the smaller sizes were more easily floated. Fluorite coarser than 65 mesh was difficult to float. The best selectivity indices were obtained with material between 65 and 150 mesh in size.

## BIBLIOGRAPHY

1. U. S. Bur. Mines Minerals Yearbook (1937).
2. F. H. Reed and G. C. Finger: Fluorspar as a Chemical Raw Material. *Chem. Ind.* (Dec. 1936) **39,** 557–581.
3. F. Medenbach: Occurrence, Production, Treatment, and Economic Importance of Fluorspar. 1935. Wetzlar: Waldschmidt.
4. H. C. Chellson: Floods versus Fluorspar. *Eng. and Min. Jnl.* (1937) **138,** 331–336.
5. R. Richards and C. E. Locke: Progress in Ore Dressing and Coal Washing. *Min. Ind.* (1925) 776–778.
6. A. F. Taggart: Handbook of Ore Dressing, 897, line 30. New York, 1927. John Wiley and Sons.
7. W. Coghill and O. Greeman: Flotation of Fluorspar Ores for Acid Spar. U. S. Bur. Mines *R.I.* 2877 (June 1928).
8. H. Madel and H. Fischer: Untersuchungen uber die Aufbereitungsmoglichkeit der sachsischen Flusspatvorkommen. *Jahrbuch* Berg und Huttenwesen (1930) 51.
9. O. Greeman and J. Williams: Recovery of Fluorspar from Ores Thereof. U. S. Patent 1785992 (Dec. 23, 1930).
10. C. Shapley: Flotation Process. U. S. Pat. 1689693 (1928).
11. W. Coghill and J. Clemmer: Soap Flotation of Nonsulfides. *Trans.* A.I.M.E (1934) **112,** 449.
12. A. M. Gaudin: Flotation, 358–369. New York, 1932. McGraw-Hill Book Co.
13. O. Greeman and H. Lilly: Flotation Process. U. S. Pat. 1926045 (Sept. 12, 1933).
14. J. Patek: Colloidal Depressors in Soap Flotation. *Eng. and Min. Jnl.* (1934) **135,** 558.

15. J. Patek: Soap Flotation. *Eng. and Min. Jnl.* (1934) **135**, 125.
16. R. O'Meara and J. Clemmer: Flotation and Depression of Nonsulfides; Calcite, Silica, and Silicates, Fluorspar, Barite, Apatite, and Tungsten Minerals. U. S. Bur. Mines *R.I.* 3239 (June, 1934).
17. K. Moser: Investigations of the Flotative Separation of Fluorite from Calcite. *Berg und Huettenm. Jahr.*, Vienna (1935) **83,** 109–112, 133–136.
18. J. G. Vail: Soluble Silicates in Industry. New York, 1928. Chemical Catalogue Company, Inc.
19. W. Halbich: New Flotation Medium. *Metall und Erz* (1933) **30,** 431.
20. Ringe and Bierbrauer: Investigation of the Flotative Separation of Barite and Dolomite. *Berg und Huettenm. Jahrb.* (1933) **81,** 139.
21. J. Sullivan: Heavy Liquids for Mineralogical Analyses. U. S. Bur. Mines *Tech. Paper* 381 (1927).
22. R. O'Meara and J. Clemmer: Methods of Preparing and Cleaning some Common Heavy Liquids Used in Ore Testing. U. S. Bur. Mines *R.I.* 2897 (1928).
23. A. Taggart: Handbook of Ore Dressing, 1214. New York, 1927. John Wiley and Sons.
24. M. N. Eigeles: Flotation of Fluorspar of the Solometchnoie District. *Mineral Suir'e* 10 (No. 10, 1935) 42–45.
25. M. N. Eigeles: Trends in Treatment of Fluorite Ores. *Gorno-Obogatitel Zhur.* (1936) No. 2, 33–42.
26. O. C. Ralston: Abstract of references 24 and 25. Can. Min. and Met. *Bull.* (1937) **40.**
27. W. E. Sinclair: Fluorspar in South Africa. *Min. Mag.* (1936) **55,** 265–270.
28. P. Hatmaker and H. W. Davis: Illinois Geol. Survey *Bull.* 59 (1938).

# A Study of the Flotative Properties of Hematite*

By W. E. Keck,† Associate Member A.I.M.E., G. C. Eggleston‡ and W. W. Lowry‡

(New York Meeting, February, 1937)

The potential iron ores of Michigan can be classified from the standpoint of the predominant impurities into siliceous, sulphurous and phosphorous ores. Research on the flotation of each of these classes of ore was carried out in the following manner. The flotative properties of the valuable minerals of iron and of the worthless and deleterious ones were first determined under carefully controlled conditions. This information was then applied to synthetic mixtures of these minerals, which simulated the potential ores. Finally, data obtained during the two foregoing stages of the investigation were used in the flotation beneficiation of samples of the potential ores.

Hematite is the most important mineral of iron in each of the above classes of iron ores. This paper deals with a study of that mineral in the very nearly pure state.

There are two varieties of the mineral—specular hematite and massive hematite. The latter is the principal variety, but the former is an important mineral of iron in some of the potential ores. Because of this condition, flotation research was performed with both varieties. This research consisted essentially of: (1) a survey of the literature on hematite flotation, (2) the preparation of pure massive hematite, (3) the preparation of pure specular hematite, (4) the development of a laboratory procedure and (5) flotation experimentation.

For the purpose of this discussion, the results of previous work on the flotative properties of hematite can be summarized as follows: Specular hematite has been readily floated with terpineol and sodium oleate or heptylic acid[1]. Further, hematite has been likewise floated with a proprietary frother and oleic acid or other soluble oils[2]. Finally, lead nitrate, copper sulphate, silver nitrate, chromium nitrate, mercuric chloride, ferric chloride, hydrochloric acid and potassium dichromate all have greatly depressed specular hematite when its flotation was attempted with sodium oleate and terpineol[1]. These data were studied, applied and enlarged upon in the present investigation.

---

* This paper describes a part of a general investigation of the flotation of Michigan's potential iron ores. A comprehensive discussion of the status of these ores and of the reasons for research on their flotation beneficiation is available in mimeographed form on application to the Michigan College of Mining and Technology, Houghton, Michigan. Issued as T. P. 763 in Mining Technology, January, 1937.

† Research Engineer, Michigan College of Mining and Technology, Houghton, Mich.

‡ Laboratory Research Assistant, Michigan College of Mining and Technology.

[1] References are at the end of the paper.

## PREPARATION OF MASSIVE HEMATITE

The pure massive hematite was prepared from two lots of high-grade iron ore (obtained from the Castile Mining Co., Ramsay, Mich.). One of the ores was soft, earthy, black in color and practically massive. Only a few minute cleavage flashes were discernible to the naked eye. The other ore was similar, except that it was slightly harder. Both ores were treated in the same way and hereafter in this paper they will be considered as one ore.

The ore was crushed with rolls to pass through 65-mesh and was then tabled several times. Tabling did not produce a marked segregation of iron in the concentrate but it did separate the slimes from the coarse material and the solid from the spongy* grains of hematite. In this way the ore was separated into slimes and three coarse materials of: (1) medium porosity (2) low porosity and (3) high porosity. The slimes were rejected insofar as the present work is concerned.

All of these coarse table products were leached with distilled water,† dried at room temperature and then separated by dry screening into −65 + 200 and −200-mesh sizes. The −200-mesh size was rejected to prevent mechanical enmeshment (in the froth) of this relatively fine material and consequent introduction of error in the flotation results.

The −65 + 200-mesh massive hematite of medium porosity was analyzed to determine whether it was sufficiently pure for the contemplated research. Only very small quantities of magnetic material, magnetite, were found in the hematite. It was concluded that the presence of this quantity of magnetite would not introduce serious error into the flotation results, magnetite being very insoluble in the usual flotation solutions and its flotative properties being quite similar to those of hematite; therefore this impurity was not removed.

Chemical analysis of the massive hematite, dried at 100° C., indicated that it contained the following quantities of materials: iron, 67.69 per cent; phosphorus, 0.053; silica, 0.77; manganese, 0.89; alumina, 0.30; lime, 0.56; magnesium oxide, 0.09; sulphur, 0.142; and volatile matter (ignition loss), 0.40. These quantities were nearly equal to the theoretical ones for hematite—70 per cent of iron and nothing of the other substances—and they indicated that the material contained approximately 96 per cent hematite.

---

* The hematite had been rendered spongy by natural leaching and removal of occluded silica.

† It was assumed that the table products were sufficiently leached when a negative qualitative test was obtained for calcium and sulfate. A pulp of 50 grams of ore and 200 c.c. of distilled water was agitated in a flotation cell for 15 min. The filtrate from this pulp was then tested for calcium and sulphate in the usual way.

A pulp was made of 50 grams of ore and 200 c.c. of distilled water (pH of 6.0). The pH of the filtrate from this pulp was 7.0.

When examined with a low-powered microscope, the material appeared to be composed entirely of hematite grains.

The results from all of these analyses indicated that the −65 + 200-mesh hematite of medium porosity was sufficiently pure* for the proposed research and it was used exclusively for all experimentation with massive hematite unless otherwise noted. Similar analyses of the −65 + 200-mesh products of low and of high porosity indicated that they were as pure as the hematite of medium porosity. These materials were used to compare the flotative properties of solid hematite with those of porous or spongy hematite. All the flotation experiments with the massive hematites described are discussed under "Experimentation."

## PREPARATION OF SPECULAR HEMATITE

The pure specular hematite was prepared from a specular iron ore (obtained by the hand picking of ore from a stockpile at Champion, Mich.), which contained approximately 80 per cent of somewhat micaceous and well crystallized hematite and smaller quantities of magnetite and quartz. This material was crushed to pass 65-mesh and was then purified by repeated tabling, which rejected nearly all the quartz. The table concentrate was leached† to further remove soluble impurities.

After being dried, the leached ore was further purified with a laboratory magnetic separator, which eliminated the magnetite in a remarkably complete manner. The product from this magnetic separator was cut into −65 + 200-mesh and −200-mesh sizes by dry screening. The −200-mesh size was rejected for the reason previously explained.

Finally the −65 + 200-mesh purified specular hematite was analyzed to determine whether it was pure enough for the contemplated research. Examination with a low-powered microscope showed that the mineral was composed almost entirely of well crystallized hematite and that it contained a negligible quantity of quartz. The filtrate obtained from a pulp of 50 grams of the mineral and 200 c.c. of distilled water (pH of 6.2) had a pH of 7.5.

---

* The analyses indicated that the massive hematite contained gypsum. However, as the mineral had been leached until a negative test was obtained for calcium and sulphate, it was concluded that the gypsum, apparently occluded in the grains of hematite, would not affect flotation. Further, the other insoluble impurities were present in small quantities, and therefore it was thought that they also would not appreciably affect flotation.

† See footnote, page 103.

Chemical analyses of the specular hematite, dried at 100° C., yielded the following results: iron, 68.51 per cent; phosphorus, 0.062; silica, 0.51; manganese, 0.03; alumina, 0.70; lime, 0.53; magnesium oxide, 0.11; sulphur, 0.016, and no volatile matter (ignition loss). These results were nearly equal to the theoretical analysis for hematite—70 per cent of iron and nothing of all the other substances—and they indicated that the material contained approximately 97 per cent specular hematite.

Study of all these analytical results led to the conclusion that the specular hematite was pure enough for the proposed research, therefore it was used for all experimentation with this mineral. Discussion concerning the purity of massive hematite (footnote, p. 104) also applies to specular hematite.

Sufficient quantities of pure massive and specular hematites having been prepared, the flotative properties of these minerals were determined in the following manner.

## Flotation Procedure

The flotation cell and technique have been described in a previous article[3]; therefore these subjects need not be discussed here except to note the following changes and additions. Froth was collected for 10 min. instead of 5, because the flotation of hematite was generally slower than that of gypsum. With massive hematite, the passing of colloidal material* through the closest filter paper often rendered the colorimetric determination of pH difficult or impossible. The difficulty was overcome by centrifuging of the suspension or, with extremely refractory samples, by filtering on a bed of coarser hematite grains.

All of the flotation reagents were chemically pure except the following: technical soluble starch, sodium silicate, ammonium laurate, ammonium linoleate, ammonium palmolate, diglycol stearate, trihydroxyethylamine stearate, trihydroxethylamine linoleate and sodium hexametaphosphate; U.S.P. gum arabic; and sodium oleyl sulfate of unknown purity.

## Presentation and Discussion of Data

The presentation and discussion of data have been described in a previous article[3] therefore the following addition need only be made at this time. The data on specular and on massive hematites are presented together to expedite comparison of their flotative properties.

## General Plan of Experimentation

The flotation of hematite was first studied with the usual nonsulphide reagents and under the other usual flotation conditions. No attempt was made to develop new reagents in this preliminary investigation except to test certain available materials, which generally were quite closely related to known reagents.

---

* From imperfect screening and especially from decrepitation of the hematite during flotation.

The flotative properties of massive and of specular hematites were observed to be quite similar in the first experiments, therefore it was assumed that parallel tendencies would also be shown under other conditions. Consequently duplicate series of experiments were not made on the two varieties of hematite, a procedure that saved considerable time and effort.

The flotative properties of hematite were principally studied with various reagents; therefore this work is classified and discussed, as far as possible, from that standpoint.

## EXPERIMENTATION

*Specular Hematite with a Frother Only.*—The floatability of specular hematite was determined with terpineol, the principal frother component of pine oil. No collection was observed with this frother, and only small quantities of fine specular hematite were carried over mechanically. In succeeding experimentation with this frother in connection with other reagents, correction was not made for the small quantity of mechanically floated hematite because it was thought that the error introduced by this procedure was negligible.

*Fatty Acid Soaps.*—The data on specular and on massive hematite are shown respectively in Figs. 1 and 2. The best flotation having been obtained with sodium oleate, the floatability of specular hematite with this collector is also shown in Fig. 2; thus the flotative properties of the two hematites can be conveniently compared. When compared with massive hematite, the only slightly greater floatability of specular hematite (with the smaller quantities of sodium oleate) probably resulted from several conditions such as: (1) greater surface area and lesser floatability with micaceous tabular mineral grains, (2) more intense flocculation and decreased floatability with a highly crystalline readily floatable mineral,* and (3) reduced floatability with a nearly complete absence of slimes.†

Other miscellaneous reagents were also tested to determine their collective properties toward hematite and to compare them with the above collectors. The results from this experimentation were as follows.

---

* This condition was especially marked because a true frother was not used in these experiments.

† When no frother was used, a small quantity of slimes was beneficial to flotation. With massive hematite, some slimes were formed from decrepitation of the mineral grains during flotation; whereas practically none were formed from the specular hematite.

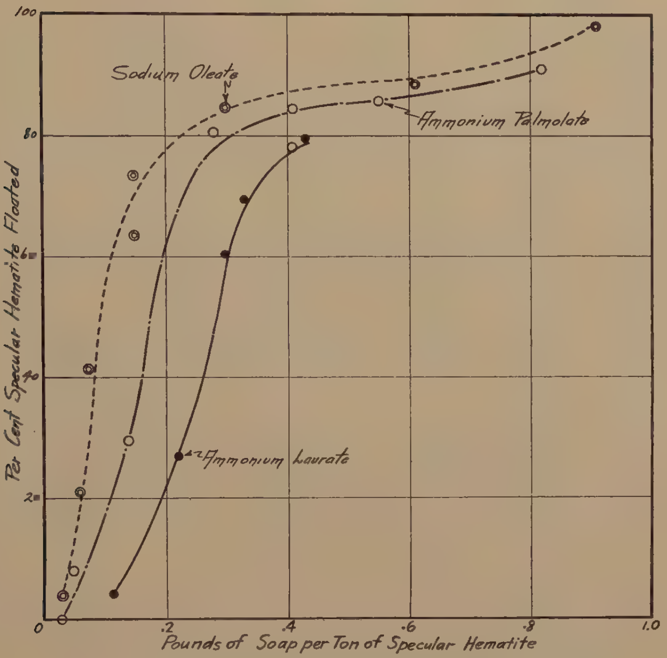


FIG. 1.—FLOTATION OF SPECULAR HEMATITE WITH SOAPS.

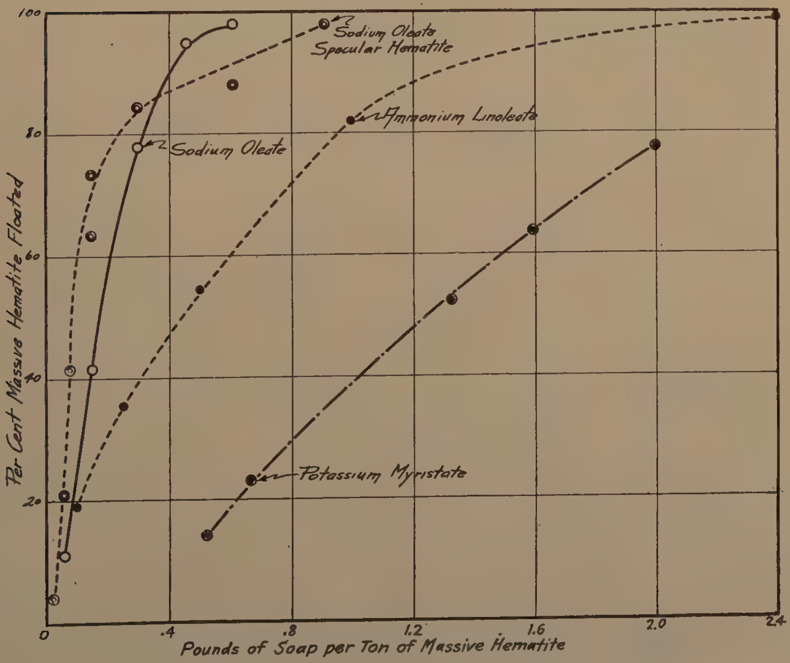


FIG. 2.—FLOTATION OF MASSIVE HEMATITE WITH SOAPS.

*Massive Hematite with Miscellaneous Collectors.*—The data from this work (Fig. 3) show that all of these reagents were collectors for hematite. However, none of them floated as much hematite as did the collectors considered in Figs. 1 and 2; therefore subsequent experimentation was confined principally to the latter materials.

*Flotative Properties of Solid and of Spongy Hematite.*—The foregoing experiments on massive hematite were performed with the product of medium porosity. It having been determined that sodium oleate is a good collector for massive hematite, the flotative properties of solid and of spongy hematite with this reagent were studied and compared, to learn whether it would be necessary to carry out parallel experiments on the products of the opposite degrees of porosity or whether continued experimentation with the product of medium porosity would yield satisfactory data.

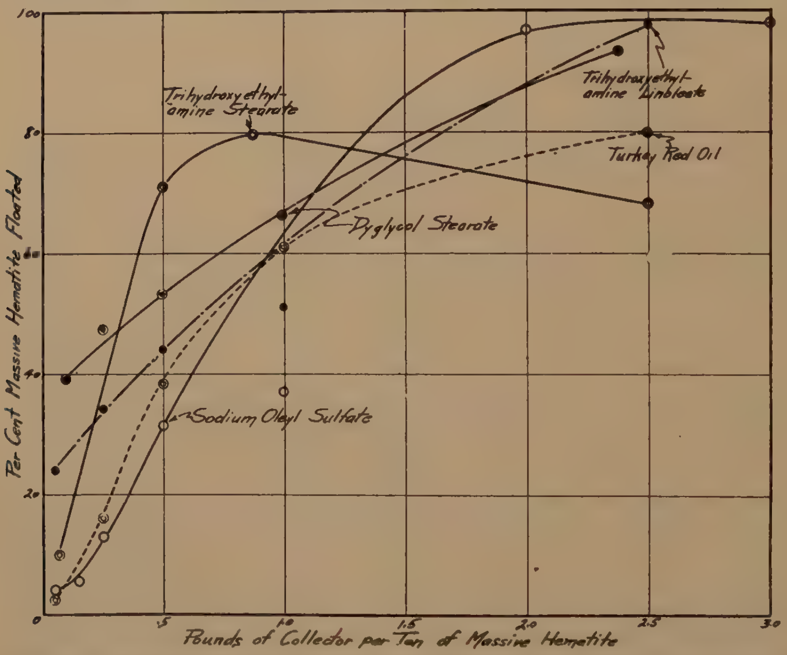


FIG. 3.—FLOTATION OF MASSIVE HEMATITE WITH MISCELLANEOUS COLLECTORS.

Massive hematite products of low and of high porosity were obtained and prepared as described above, the resultant distributions of sizes being those shown in columns A of Table 1. Parallel experiments on these materials (columns A) gave the results shown in Fig. 4.

Next, the two massive hematite products were sized by wet screening. The several sizes were dried, weighed, and then so combined that both of the products contained equal quantities of each size as shown in columns B of Table 1. When the products under columns B were tested with 0.3 lb. sodium oleate, 45 per cent of the solid and 49.5 per cent of the spongy hematite were floated with this treatment.

TABLE 1.—*Distribution of Sizes in Solid and Spongy Massive Hematite Products*

PER CENT WEIGHT

| Size Range, Mesh | Solid Hematite | | | Spongy Hematite | | |
|---|---|---|---|---|---|---|
| | A | B | C | A | B | C |
| − 65 + 80 | 23.5 | 20.4 | 15.9 | 22.0 | 20.4 | 15.9 |
| − 80 + 100 | 32.5 | 29.4 | 18.9 | 30.6 | 29.4 | 18.9 |
| −100 + 150 | 25.7 | 26.5 | 25.2 | 25.0 | 26.5 | 25.2 |
| −150 + 200 | 18.3 | 23.7 | 40.0 | 22.4 | 23.7 | 40.0 |

Further experiments were performed with the massive hematite products of columns B. Samples of both products were immersed in distilled water for 110 hr. and then floated, as before, with 0.3 lb. sodium oleate. Under these conditions, 47.5 and 36.5 per cent of the solid and of the spongy hematite respectively were floated. Compared with previous experiments, nearly the same quantity of solid hematite was floated, but spongy hematite was considerably depressed. Depression probably was due to filling of the spongy hematite pores with water, which increased the

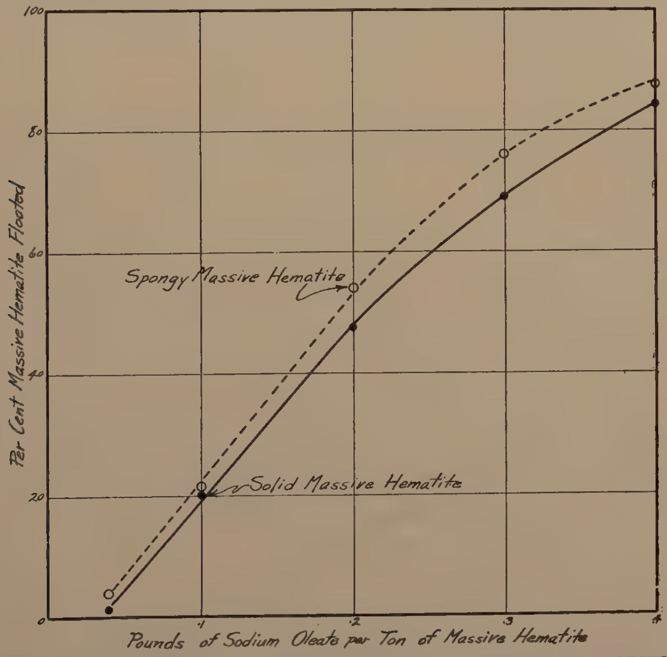


FIG. 4.—FLOTATION OF SOLID AND SPONGY MASSIVE HEMATITE WITH SODIUM OLEATE.

apparent density of the mineral. This condition tended to depress, especially because a considerable portion of the hematite grains approached the upper size limit of floatability.

Finally, the two hematite materials were made with the size distribution shown in columns C of Table 1. Then these products were tested with 0.3 lb. of sodium oleate; 57.5 per cent of the solid and 49.5 per cent of the spongy hematite were floated with this treatment.

From these data, it appeared that two opposing tendencies were present in the flotation system. The spongy condition of the massive hematite tended: (1) to increase the surface area of the mineral and depress its flotation with a given quantity of collector, and (2) to decrease the apparent specific gravity of the mineral grains and to increase floatability when other conditions were equal. With a larger percentage of the coarse grain sizes (columns A and B), the latter tendency was stronger, and with a larger percentage of the fine grain sizes (column C) the former tendency predominated. These observed phenomena appear logical when it is considered: (1) that the coarse grains were near the upper size limit of flotation and (2) that the surface area increases greatly with decrease in grain size.

It was further concluded that, under usual conditions, there was no marked difference in the floatability of the massive hematites of low (solid), medium or high porosity (spongy). Consequently all succeeding experimentation on massive hematite was carried out with the hematite of medium porosity that already had been used to obtain the results shown in Figs. 2 and 3.

*Specular Hematite with Fatty Acids.*—The floatability of specular hematite with several fatty acids is shown in Figs. 5 and 6. The fatty acids were added to the pulp in alcoholic solution, and the experiments were conducted at room temperature. With the saturated fatty acids, flotation increased with the number of carbon atoms until a maximum of 12 carbon atoms was reached; thereafter, flotation apparently decreased, with further increase in number of carbon atoms.

Because oleic acid was the best collector, further experimentation with the fatty acids was confined to it.

*Massive Hematite with Oleic Acid and Sodium Hydroxide or Carbonate.* These experiments were performed: (1) to determine the effect of increase in alkalinity on the flotation with oleic acid and (2) to compare the collecting powers of sodium oleates formed within* and without the flotation system.

The data from these experiments are shown in Fig. 7. Activation with the smaller quantities of the bases was perhaps due to superior

---

[*] For the sake of simplicity, it is assumed that the oleic acid reacted chemically with sodium hydroxide to form sodium oleate; actually other products in addition to sodium oleate probably were present in both cases listed as 2.

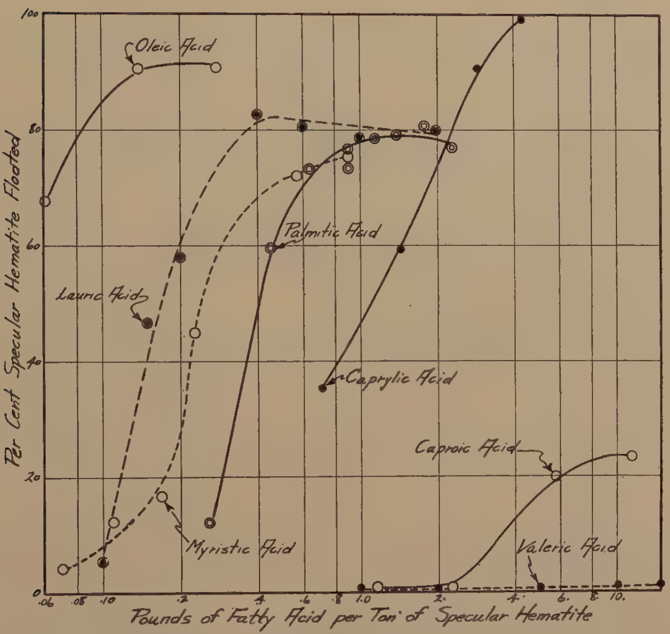


FIG. 5.—FLOTATION OF SPECULAR HEMATITE WITH FATTY ACIDS. Quantities of acids expressed in pounds per ton.

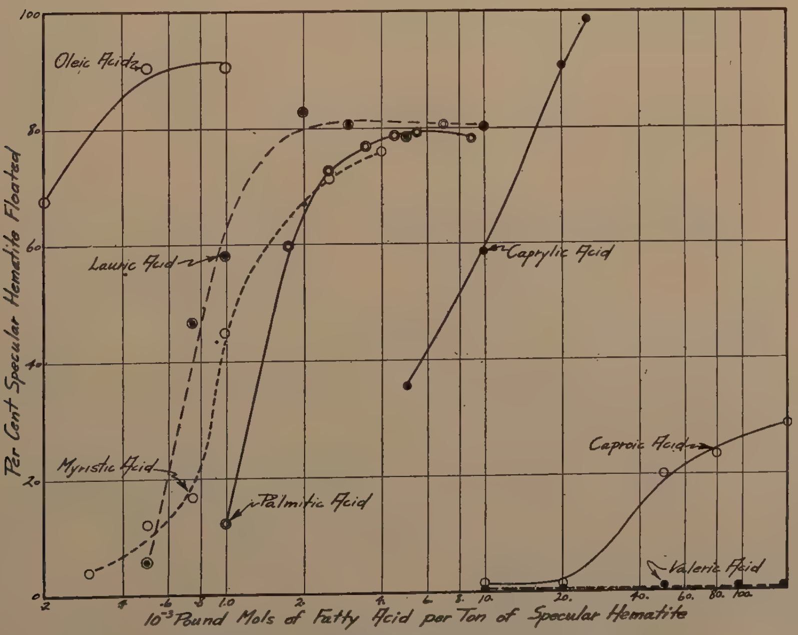


FIG. 6.—FLOTATION OF SPECULAR HEMATITE WITH FATTY ACIDS. Quantities of acids shown in pound mols per ton.

dispersion of the oleic acid. Improved dispersion was obtained by the formation of emulsions and soluble compounds from sodium hydroxide and oleic acid.

Sodium oleate that was formed in contact with the hematite floated slightly more of the mineral than did sodium oleate that was added as such to the flotation system. Maximum flotation in the former case with 0.05 lb. oleic acid was approximately 60 per cent;* whereas flotation with 0.054 lb. of sodium oleate† (stoichemetric equivalent of 0.05 lb. oleic acid) was 52.6 and 51.8 per cent, or an average of approximately 52 per cent of complete flotation.*

Although oleic acid was slightly superior to sodium oleate, experimentation was continued with the latter reagent only because it was thought that the use of oleic acid in alcoholic solution possibly introduced a complicating factor in the flotation system.

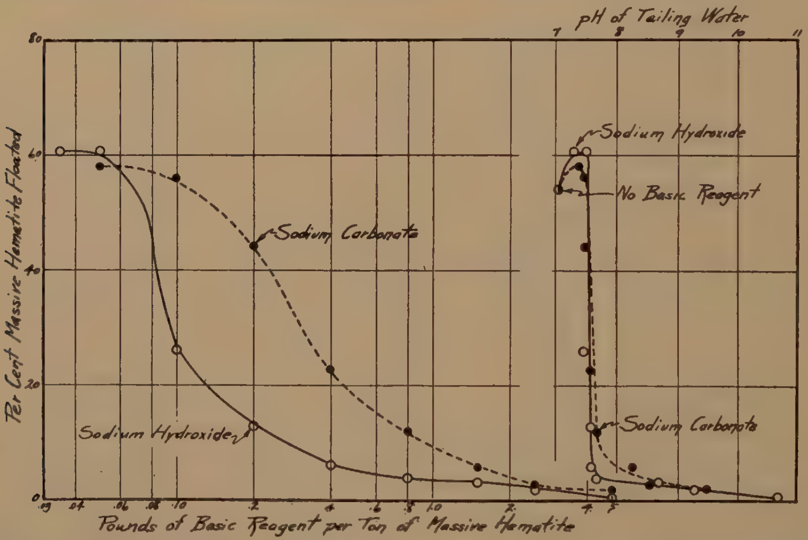


FIG. 7.—EFFECT OF SODIUM HYDROXIDE AND SODIUM CARBONATE ON FLOTATION OF MASSIVE HEMATITE WITH 0.05 LB. OLEIC ACID AND 0.10 LB. TERPINEOL.

*Massive Hematite with Sodium Oleate and Frothers.*—A frother is generally used in connection with fatty acids or soaps in the flotation of nonsulphides. This practice was studied in relation to the present problem. Cresylic acid, terpineol and n-heptyl alcohol were used in this study for the following reasons: Cresylic acid is a widely applied frother; terpineol is the principal frothing component of pine oil, another widely used frother; and the use of n-heptyl alcohol gave good results in previous experimentation[3].

---

* The pH values of the tailing water were from 7.0 to 7.1.

† Sodium oleate solution used in these experiments was freshly made.

The data from these experiments (Figs. 8 and 9) show that: (1) the addition of the frothers, in usual quantity, greatly increased the flotation of massive hematite, (2) when compared on a pound basis, terpineol and n-heptyl alcohol are about equally effective and both of these frothers are markedly superior to cresylic acid and (3) when compared on a molecular basis, terpineol is somewhat more potent than n-heptyl alcohol, and the relative frothing powers of n-heptyl alcohol and cresylic acid are approximately the same as under 2 above.

When sodium oleate only was used, the quantity of this reagent available for frothing was not sufficient for good flotation. Addition of a frother, which was not consumed by the hematite, greatly increased frothing and consequently also increased flotation. The results with cresylic acid were inferior, because it probably was too soluble for best frothing; whereas the solubilities of terpineol and n-heptyl alcohol more nearly approached the solubility optimum for frothing. The solubilities of these frothers are as follows: ortho, meta and para cresol, 24.5, 21.8 and 19.4 grams, respectively, per liter of saturated solution at 20° C.[4]; alpha and beta terpineol, 1.98 and 2.20 grams respectively per liter of saturated solution at 15–20° C.[5]; and n-heptyl alcohol approximately one gram per liter at 18° C. (ref. 5, 1228).

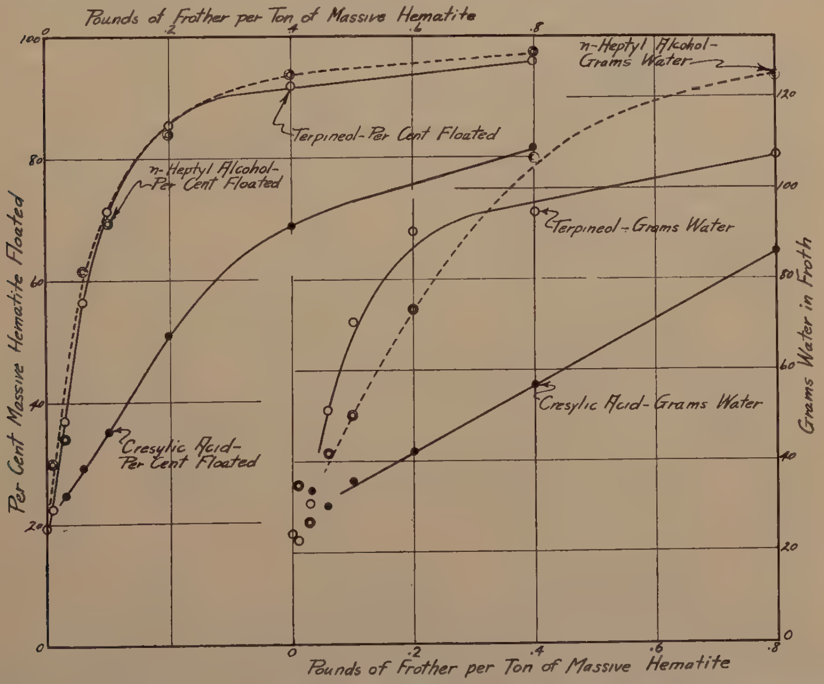


FIG. 8.—FLOTATION OF MASSIVE HEMATITE WITH FROTHERS AND 0.10 LB. SODIUM OLEATE.

Water in froth. Quantities of frothers in pounds per ton.

Because these experiments indicated that terpineol was somewhat superior to n-heptyl alcohol, and because it is the principal component of a widely used frother, terpineol was used exclusively in succeeding investigation.

*Grain Size and Floatability.*—The data from this work (Fig. 10) indicate: (1) that massive hematite was practically unfloatable at −35 + 48-mesh, (2) that maximum floatability occurred between −200 and +325-mesh and (3) that massive hematite ores must be ground to pass at least through 65 mesh to float the hematite under the conditions in question.

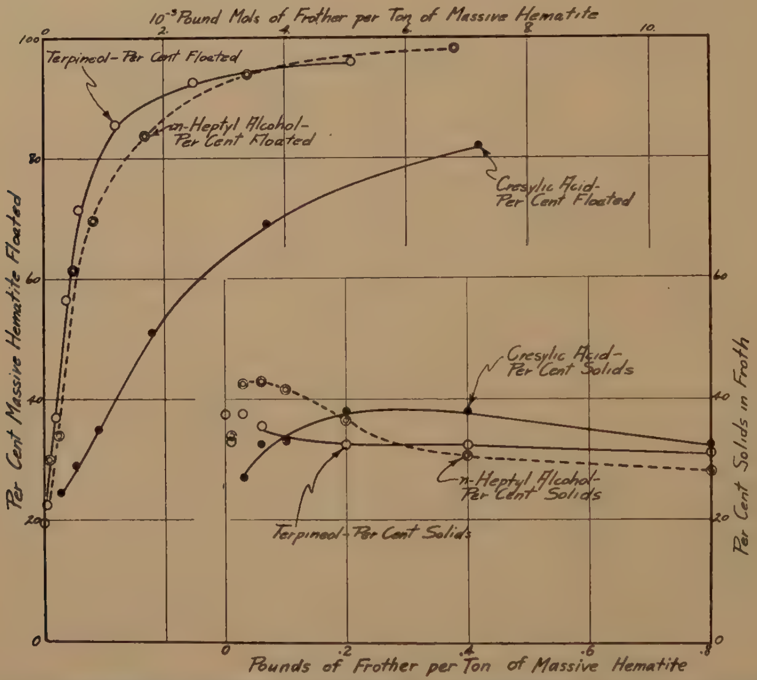


FIG. 9.—FLOTATION OF MASSIVE HEMATITE WITH FROTHERS AND 0.10 LB. SODIUM OLEATE.

Per cent solids in froth. Frother quantities expressed in pound mols per ton.

Preliminary tests with sodium metaphosphate showed that it activated the flotation of coarse hematite; consequently the finer sizes were also used in experimentation with this reagent. The results of this work are also shown in Fig. 10. Addition of sodium metaphosphate did not change the pH of the tailing water, but did cause an increase of approximately 10 per cent in the quantity of froth. Depression of the finer sizes was perhaps connected with the deflocculative action of sodium metaphosphate, intense deflocculation being an outstanding phenomenon of all experiments in which this reagent was used.

Conclusions having been reached in regard to the best collector and frother and the maximum grain size, experimentation was continued to determine the optimum pH condition.

*Massive Hematite with Sodium Oleate and Acidic or Basic Reagents.*—The results of this work are shown in Figs. 11 and 12. Under basic conditions with sodium hydroxide, the quantity of froth was always considerably greater than without sodium hydroxide at the neutral point. Thus depression of the hematite with the larger quantities of the base was not due to lack in the quantity of froth.

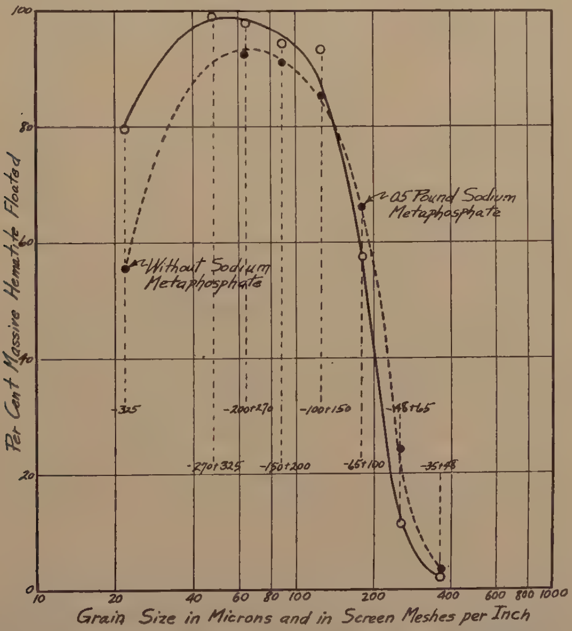


FIG. 10.—RELATION BETWEEN GRAIN SIZE AND FLOATABILITY.
Effect of sodium metaphosphate on flotation of different grain sizes. Massive hematite floated with 0.40 lb. sodium oleate and 0.10 lb. terpineol.

With very small quantities of sodium hydroxide and with very small increase in pH, flotation of the hematite was activated considerably. At a pH value of approximately 9 an unknown activating factor was indicated both by the pH per cent floated curve (Fig. 11) and by an increase in quantity of froth. However, this activating tendency was not strong enough to overcome the depressing one; consequently, the resultant of the two tendencies was a marked reduction in flotation.

With sodium carbonate, depression of flotation and frothing were parallel; consequently, it cannot be said whether depression was due to interference with collection, to interference with frothing, or to a combination of these factors.

When lime was added, frothing was not reduced to the same extent as was the flotation of hematite, considerable frothing being observed when the hematite was completely depressed. Depression perhaps was caused by the formation and nonadsorption of calcium oleate on the surface of the hematite grains. It is of interest to the present consideration that a marked depression was also observed with calcium nitrate and sulphate (see p. 117).

Under acidic conditions between the pH values of 6.7 and 4.5, the quantity of froth was equal to or greater than the quantity at the neutral point. Thereafter, with increasing acidity frothing was reduced, until with pH values of 2 or less it was entirely depressed. These data indicate that the greater part of the hematite depression was not due to lack in quantity of froth. The effect of acidic and alkaline conditions on the flotation of hematite having been determined, search was made to discover activators for flotation of the mineral.

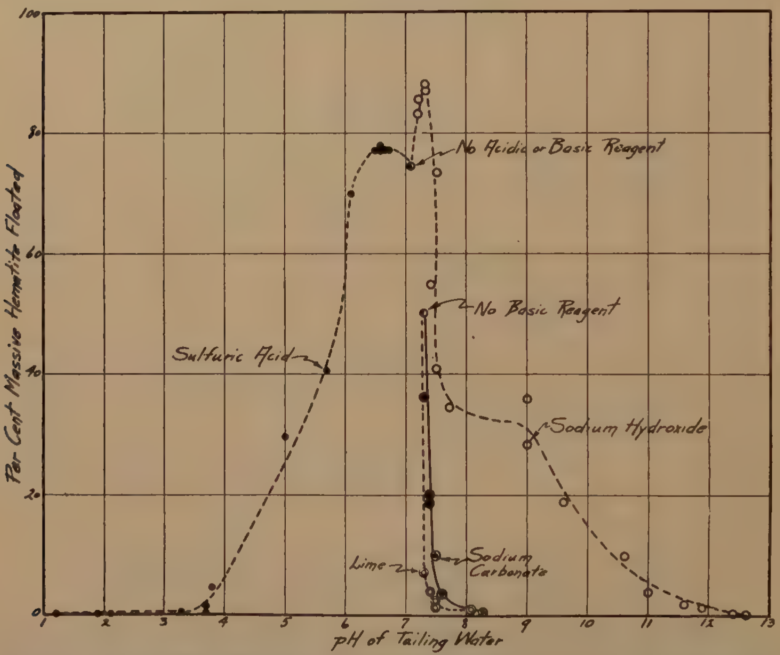


FIG. 11.—RELATION BETWEEN pH AND FLOATABILITY OF MASSIVE HEMATITE. Sodium hydroxide and sulphuric acid with 0.20 sodium oleate and 0.1 lb. terpineol. Sodium carbonate and lime with 0.05 lb. sodium oleate and 0.10 terpineol.

*Massive Hematite with Sodium Oleate and Metal Salts.*—The data from the metal salts have been separated into and are shown graphically in two groups to facilitate their inspection and discussion. The data of the first group are shown in Figs. 13 and 14 and those of the second group are shown in Figs. 15 and 16. In addition, the pH values of the

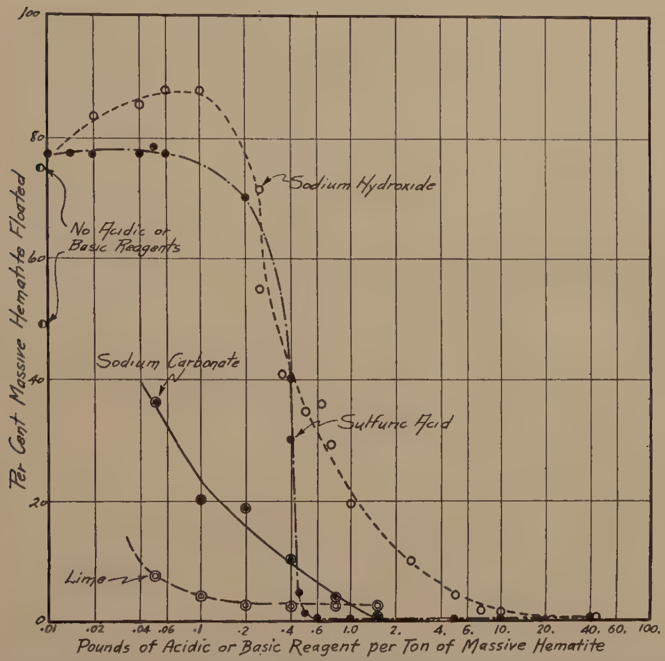


FIG. 12.—EFFECT OF ACIDIC AND BASIC REAGENTS ON FLOTATION OF MASSIVE HEMATITE.

Sodium hydroxide and sulphuric acid with 0.20 lb. sodium oleate and 0.10 lb. terpineol. Sodium carbonate and lime with 0.05 lb. sodium oleate and 0.10 lb. terpineol.

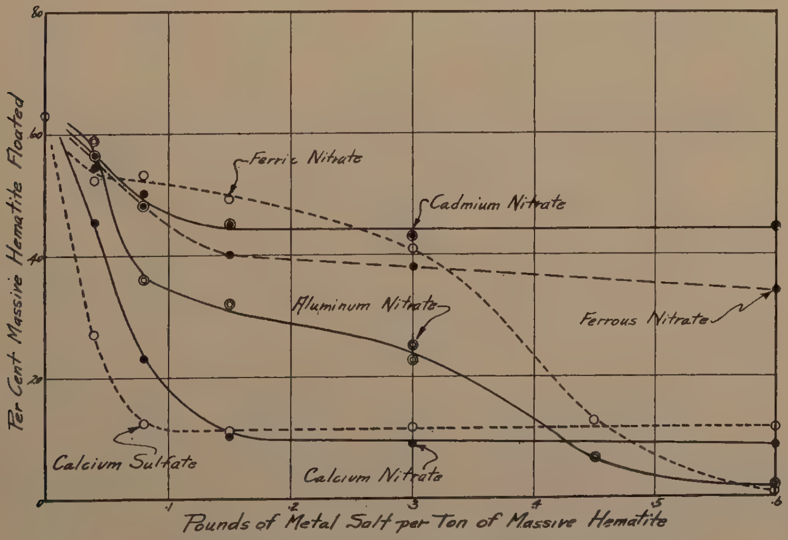


FIG. 13.—FLOTATION OF MASSIVE HEMATITE WITH 0.20 LB. SODIUM OLEATE AND METAL SALTS.

Quantities of metal salts in pounds per ton.

tailing water from all experiments are given in Fig. 17. From a comparison of Fig. 17 with Fig. 11, it appears that depression and activation

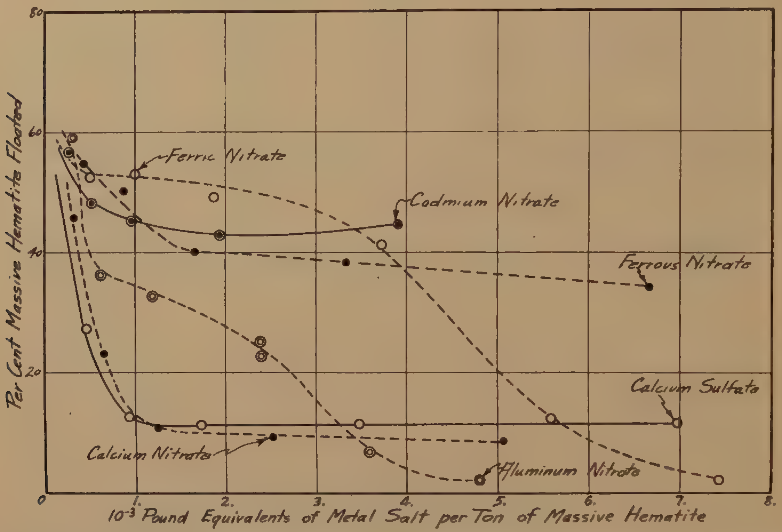


FIG. 14.—FLOTATION OF MASSIVE HEMATITE WITH METAL SALTS AND 0.20 LB. SODIUM OLEATE.

Quantities of metal salts in pound equivalents per ton.

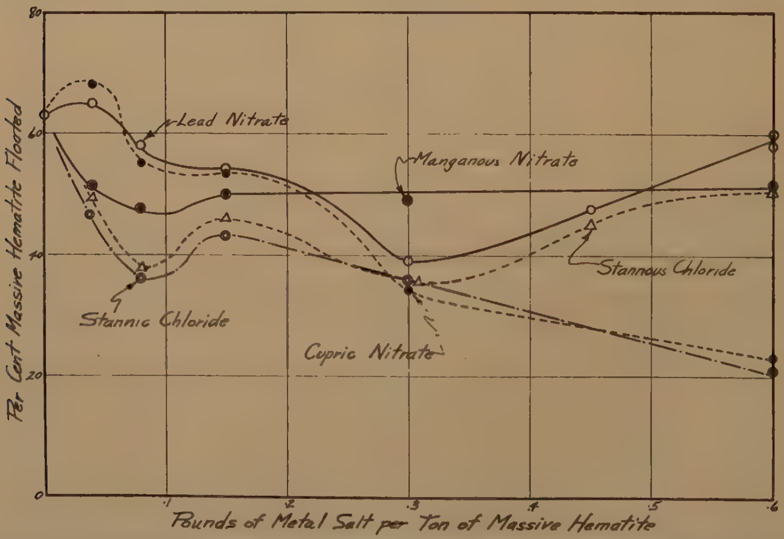


FIG. 15.—FLOTATION OF MASSIVE HEMATITE WITH METAL SALTS AND 0.20 LB. SODIUM OLEATE.

Quantities of metal salts in pounds per ton.

with the metal salts came largely from factors other than the decrease of pH.

Because of lack of solubility data on the metal soaps in question, the results obtained with the metal salts cannot be discussed from this standpoint. The curves of Figs. 15 and 16 show alternate activation and depression.* Of interest in connection with this subject is Trillat's

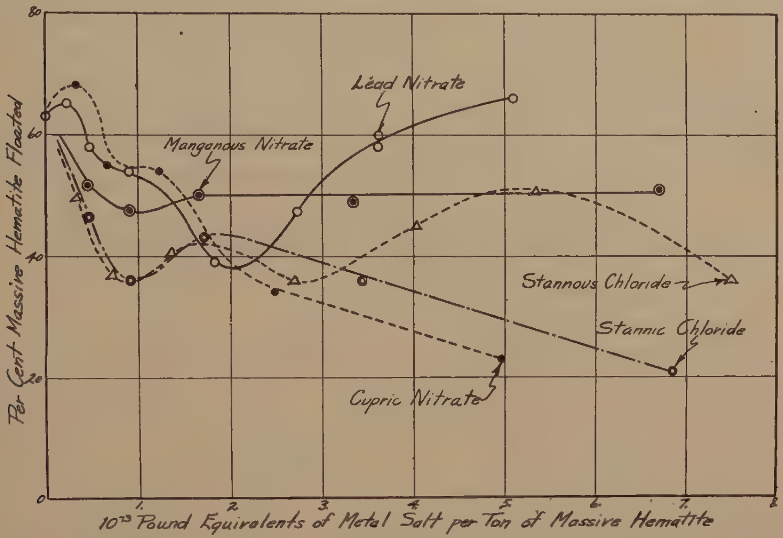


FIG. 16.—FLOTATION OF MASSIVE HEMATITE WITH 0.20 LB. SODIUM OLEATE AND METAL SALTS.

Quantities of metal salts in pound equivalents per ton.

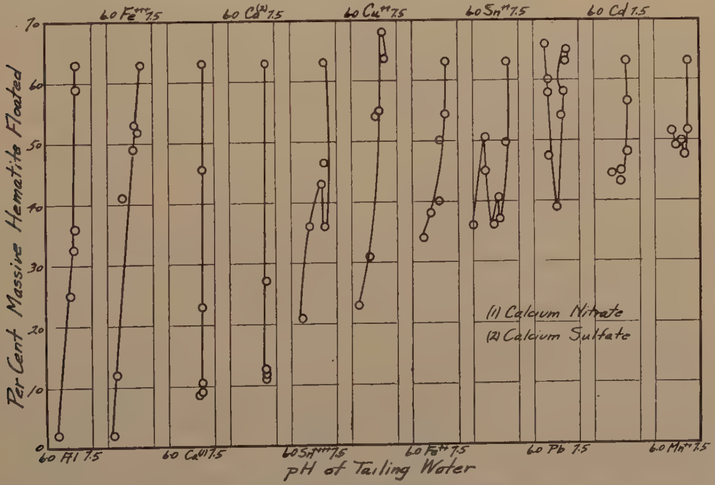


FIG. 17.—pH OF TAILING WATER. MASSIVE HEMATITE FLOATED WITH 0.20 LB. SODIUM OLEATE AND METAL SALTS.

---

* Activation and depression were not outstanding with each salt, nevertheless indications of these phenomena were present in each case. Further, parts of the curves undoubtedly were not determined because an insufficient number of points was obtained on them.

study of fatty acids placed on metal plates; in this research intense metal-soap spectra were obtained on lead, tin and antimony; less intense spectra on bismuth, copper and iron, and none at all on aluminum[6]. Further, the successive layers of molecules were orientated as follows: metal plate: metal OOCR:RCOOH:HOOCR, and so on, until 100 to 200 lamina of double layers of molecules were built up[7]. Of interest also is Rehbinder's conclusion that depression with an excess of reagent is due to the reversed orientation of the collector molecules[8].

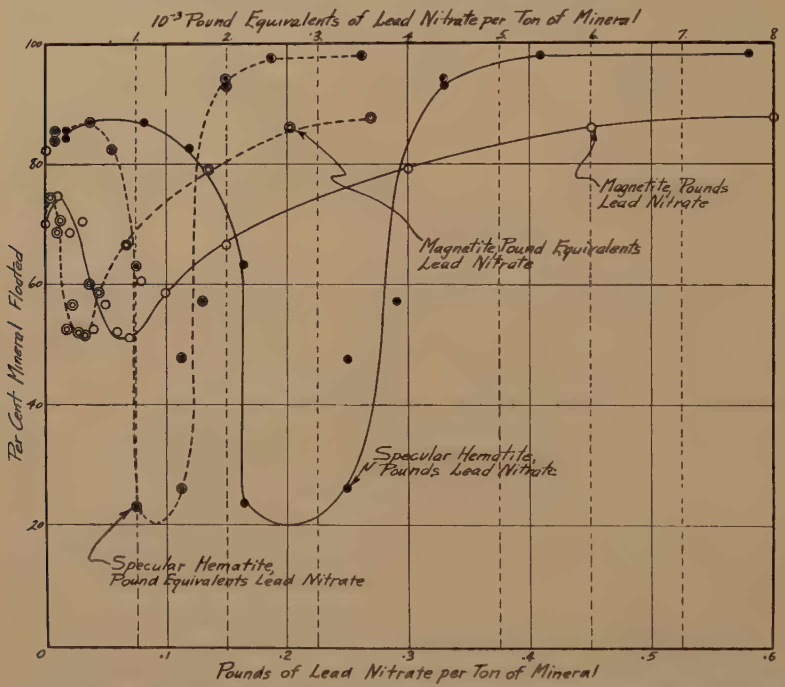


FIG. 18.—FLOTATION OF SPECULAR HEMATITE AND MAGNETITE WITH 0.30 LB. SODIUM OLEATE AND LEAD NITRATE.

Orientation of the molecules of metal soaps (from the metal salts and sodium oleate) on the surface of the hematite perhaps was similar to that of the metal soaps and fatty acid molecules on metal plates. Thus the mineral was alternately water-repellent and water-avid, and the observed activation and depression of flotation are readily explained.

Assuming that this phenomenon would be more marked on crystalline minerals than on massive ones, its study was continued with experimentation on specular hematite.

*Specular Hematite with Sodium Oleate and Lead Nitrate.*—Lead nitrate was used for this work because marked activation and depression were obtained with it in the experiments described above. The experimental findings are given in Fig. 18. For the sake of additional experimental evidence on this subject, and because the flotative properties of magnetite were found to be quite similar to those of specular hematite, the data from a series of experiments on a sample of the pure, well crystallized mineral are also shown in Fig. 18.

The results shown in Fig. 18 resemble those of Figs. 15 and 16 except that activation and depression in the former case are somewhat more pronounced than in the latter one. The discussion of the results shown in Figs. 15 and 16 also applies to those given in Fig. 18.

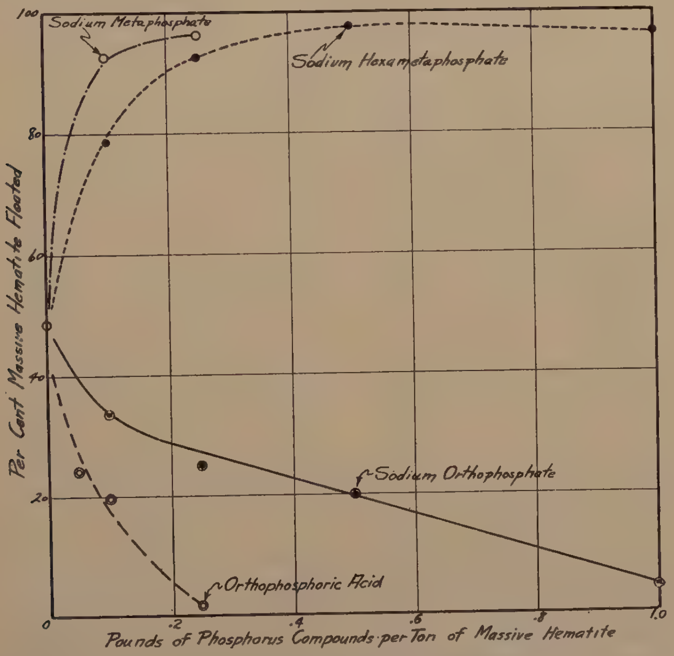


FIG. 19.—EFFECT OF PHOSPHORUS COMPOUNDS ON FLOTATION OF MASSIVE HEMATITE WITH 0.15 LB. SODIUM OLEATE.

Flotation with the metal salts was extremely sensitive to change in quantity of the metal salt, and further study of the subject has indicated that the quantity of collector (constant for each series) also had a marked effect on the shape of the curves with varying quantities of metal salts. Continued work with more precise methods of experimentation undoubtedly is necessary for a thorough study of the subject.

These experiments concluded the work with metal salts. The investigation was continued with a search for other activators of hematite.

*Massive Hematite with Sodium Oleate and Phosphorus Compounds.*—It was found that sodium metaphosphate was an activator for hematite; therefore several other phosphorus compounds were also tested. The data from this work (Fig. 19) indicate that sodium meta and hexametaphosphate* were powerful activators and that sodium orthophosphate and orthophosphoric acid were depressors for the flotation of massive hematite with sodium oleate.

Sodium meta and hexametaphosphate did not materially effect the pH of the tailing water; whereas sodium orthophosphate and orthophosphoric acid reduced the pH respectively to 6.6 (1.0 lb. per ton) and 6.5 (0.25 lb. per ton). Comparison of these results with those of Fig. 11 indicates that activation and depression with the phosphorus compounds apparently were not due to changes in pH. Further, the meta and ortho compounds differ in the degree to which their molecules polymerize—perhaps their diametrically opposite effects in flotation result from this difference in physicochemical properties. Study of this subject was continued with sodium hexametaphosphate and several collectors in addition to sodium oleate.

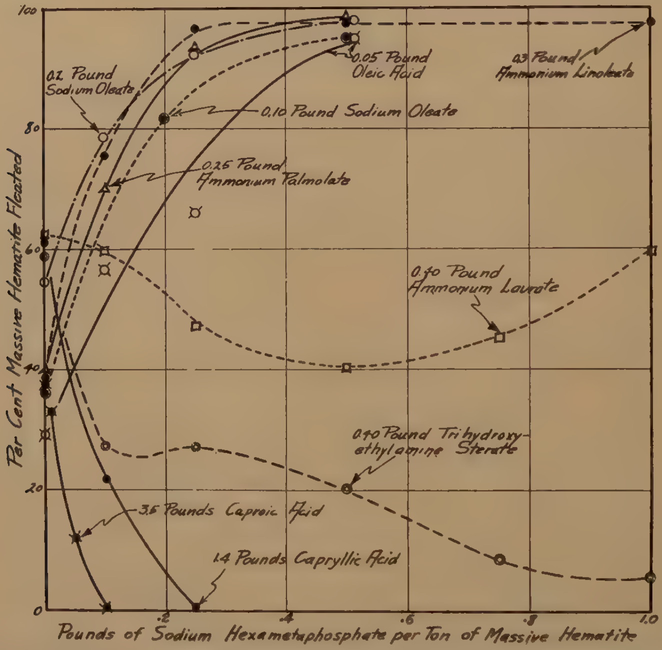


FIG. 20.—FLOTATION OF MASSIVE HEMATITE WITH SODIUM HEXAMETAPHOSPHATE AND SEVERAL COLLECTORS.

*Massive Hematite with Sodium Hexametaphosphate and Several Collectors.*—The data from this work (Fig. 20) show that the nature of the collector greatly affected the results obtained with sodium hexametaphosphate. Activation was observed with all of the unsaturated collectors;* whereas little effect or depression was obtained with the saturated collectors. More investigation is necessary to determine whether: (1) the presence of the double bond in the collector is fundamental in the activation with sodium hexametaphosphate or (2) whether the solubilities of the iron oleates and phosphates entered into the observed activation and depression.

---

* A technical product containing 99 per cent sodium hexametaphosphate. The authors are indebted to Mr. G. W. Smith, Calgon, Inc., for samples of and description of this material.

This research was concluded with a series of experiments on massive hematite with sodium oleate and some colloidal reagents.

*Massive Hematite with Sodium Oleate and Colloidal Reagents.*—The practice of depressing gangue minerals with sodium silicate or soluble starch was studied in relation to the flotation of massive hematite. The results of this study with these and three other colloidal materials are shown in Fig. 21.

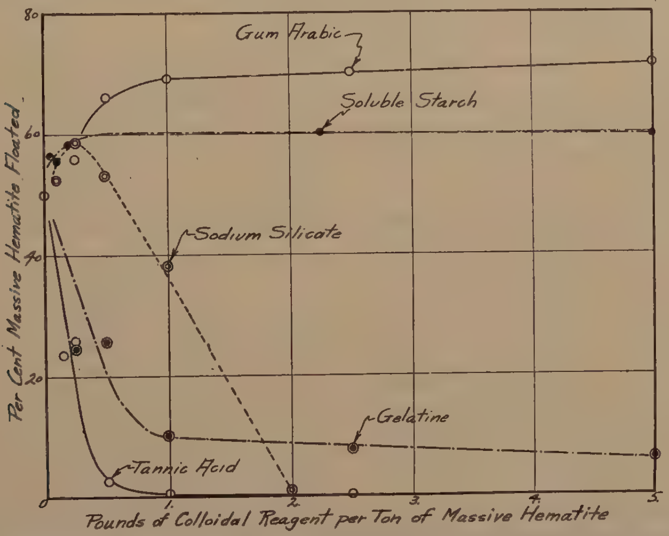


FIG. 21.—FLOTATION OF MASSIVE HEMATITE WITH COLLOIDAL REAGENTS AND 0.15 LB. SODIUM OLEATE.

Because of extreme deflocculation, the pH values of the tailing were not determined for the experiments with sodium silicate. However, depression with the larger quantities of sodium silicate perhaps came partly at least from the increase of pH that generally accompanies the addition of sodium silicate.

---

* Ammonium palmolate is an ammonium soap prepared from palm oil. (The authors are indebted to Mr. E. Rosendahl of Glyco Products Co., Inc. for this information.)

The mixed fatty acids from commercial palm oils contained from 33 to 41 per cent palmitic acid, 41 to 50 per cent oleic acid and 8 to 10 per cent of linolenic acid[9]. Thus the ammonium palmolate used in the present experimentation undoubtedly contained unsaturated ammonium soaps.

The experiments with the colloidal reagents concluded this general study of the flotative properties of hematite. Data from this experimentation have been applied to the flotation of samples of potential ores that contained an excess of silica or sulphur. This work will be published in the near future.

## Summary and Conclusions

The flotative properties of massive and specular hematite were studied because these minerals are the principal sources of iron in the potential iron ores of Michigan. Relatively pure natural massive and specular hematite were used in this study.

Both massive and specular hematite were readily floatable with the following fatty acid soaps: sodium oleate, ammonium palmolate, potassium myristate, ammonium linoleate and ammonium laurate. Among these soaps, sodium oleate was the strongest collector.

Massive hematite was also floated with trihydroxyethylamine stearate, trihydroxyethylamine linoleate, diglycol stearate, Turkey Red oil and sodium oleyl sulphate, but these miscellaneous collectors were not as potent as the fatty acid soaps.

Specular hematite was slightly more floatable than massive hematite. Comparison of the flotation of solid hematite with that of spongy hematite indicated that the former was somewhat more floatable in the fine sizes and the latter more floatable in the coarse sizes.

When specular hematite was floated with the saturated fatty acids, flotation was first increased and then depressed with increasing number of carbon atoms.

The use of increasing quantities of sodium hydroxide or carbonate with oleic acid first slightly activated and then markedly depressed the flotation of massive hematite.

Sodium oleate that was formed within the flotation system floated somewhat more massive hematite than did sodium oleate that was added to the system as such.

Small quantities of cresylic acid, terpineol or n-heptyl alcohol greatly increased flotation with sodium oleate. Terpineol and n-heptyl alcohol were considerably better frothers than was cresylic acid.

Massive hematite was most floatable at $-200 + 325$-mesh, somewhat less floatable at $-325$-mesh, and practically unfloatable at $-35 + 48$-mesh.

Sodium metaphosphate activated flotation with the coarse sizes of massive hematite and depressed it with the fine sizes.

The flotation of massive hematite was strongly depressed with sodium carbonate and lime. Increasing quantities of sodium hydroxide or sulphuric acid first activated flotation slightly and finally completely depressed it.

Hydrous calcium sulphate depressed hematite when its flotation was attempted with sodium oleate.

Sodium meta and hexametaphosphates strongly activated the flotation of massive hematite, and sodium orthophosphate and orthophosphoric acid depressed it. Sodium hexametaphosphate activated flotation when used with unsaturated fatty acids or soaps and had little effect or depressed flotation when used with saturated collectors.

Tannic acid, gelatin and sodium silicate were potent depressors for massive hematite. On the other hand, gum arabic and soluble starch slightly activated flotation of the mineral.

## Acknowledgments

Grateful acknowledgment is made of the aid which the authors received in this work. They are especially indebted to G. C. Dillman, President, to N. H. Manderfield and C. T. Eddy, Associate Professors of Metallurgy, and T. M. Broderick, Research Professor of Geology, of the Michigan College of Mining and Technology. The services of laboratory assistants were provided under Project 31-F2-59 as a part of a cooperative research program sponsored by the Federal Emergency Relief Administration.

## References

1. A. M. Gaudin and H. Glover: Flotation Fundamentals, I, 97. Univ. of Utah, 1928.
2. R. S. Dean and A. B. Hersberger: New Flotation Reagents. Page 81, this volume.
3. W. E. Keck and P. Jasberg: A Study of the Flotative Properties of Gypsum. *Trans.* A.I.M.E. (1938) **129**, 218.
4. Seidell: Solubilities of Inorganic and Organic Compounds, Ed. 2, 278. New York, 1918. D. Van Nostrand Co.
5. Seidell: Supplement to Solubilities of Inorganic and Organic Compounds, 1466. New York, 1928.
6. J. J. Trillat: Study of Soaps and Fats by X-rays. *Chem. Absts.* (1925) **19**, 2764.
7. J. J. Trillat: Modern Views of Friction. *Chem. Absts.* (1929) **23**, 3847.
8. P. Rehbinder et al.: Physical Chemistry of Wetting Phenomena and Flotation. *Chem. Absts.* (1934) **29**, 1907.
9. H. K. Dean and T. B. Hilditch: Composition of Commercial Palm Oils, III. *Chem. Absts.* (1933) **27**, 3839.

## DISCUSSION

[This discussion refers also to the paper that begins on page 129.]

(*Arthur F. Taggart presiding*)

W. E. Keck.—In considering the problem of the potential iron ores of Michigan, it was assumed, of course, that Michigan would continue to produce iron ore, after the high-grade ores had been exhausted, from the low-grade or the potential material, and that these low-grade materials would require dressing. The problem was begun at the Michigan College of Mining and Technology in 1926. The first few years of experimentation consisted mostly of gravity concentration. After several years of that work, the following conclusions were reached: (1) that the favorably banded or textured low-grade siliceous ores can be concentrated by gravity methods; (2) that these concentration processes produce fines and middlings that cannot be worked by that same process; (3) that in some cases the coarser textured or gravity-amenable members of a formation are separated by others that are finer textured and will not respond to gravity concentration methods. If these coarsely textured members were considered alone, each would have to be mined by underground methods, whereas if some way were worked out by which the finer textured members could also be treated, the whole formation could be mined by open-cut methods.

Taking the potential ores as a whole, the greater portion was finely textured and could not be treated by gravity methods; also, there are some high-sulphur and high-phosphorus ores that are very finely textured and do not respond to gravity concentration. The latter classes of ores are very attractive from one standpoint; that is, the iron content is satisfactory just as they are and the deleterious mineral content is generally under 5 per cent, so that we could logically hope for a very good yield of finished concentrate from these materials. Instead of having to handle two or more tons of raw material for one ton of finished concentrate, we would probably have to handle slightly more than one ton. In addition, large blocks of this material had been developed incidentally while search was being made for material of a low sulphur or a low phosphorus content.

All of the conditions just enumerated indicated the need of some method that was applicable to these finely textured ores. Needless to say, flotation was thought of at once, because it has been successfully applied to many finely textured nonferrous and nonmetallic ores. To avoid misunderstanding, we do not maintain that flotation is economically feasible at the present time or will be when the beneficiation of Michigan ores finally comes into general practice. On the other hand, we do believe that flotation has possibilities and is worthy of investigation.

A. F. TAGGART,* New York, N. Y.—In the flotation tests, was a gangue present or was magnetite, hematite and gypsum, respectively, only present in the cell.

W. E. KECK.—The pure minerals only were present in the cell.

A. F. TAGGART.—In the high-sulphur ores, do you float gypsum or hematite?

W. E. KECK.—The gypsum has been floated thus far. We should have liked very much to do it the other way, but we have not been able to accomplish it thus far.

A. F. TAGGART.—There is smaller bulk to float in floating the gypsum.

W. E. KECK.—In some places there is silica to be considered also.

M. L. GRIFFIN,† Taunton, Mass.—May I ask if the author of this paper drew any general conclusions from his experiments whereby he could predict the results generally on alkaline earth minerals such as gypsum and limestone? I have in mind the difference in choice of reagents. Has he been able to draw any universal conclusions as to the reagent to be used? The results, of course, depend largely upon the pH of the reacting medium.

W. E. KECK.—Combining this with other work, I have found that where there is a strong base in a mineral, it generally will be activated by an alkaline condition. I have noted that in at least two other instances. With gypsum, the activation occurred at too great alkalinity to be practical, but there is one other case that I recall where it occurred at a pH of 10 or 11, and it finally was made the basis of a process, separation of a nonmetallic from sulphides and other gangue. It kept all the sulphides down and floated the nonmetallic.

---

* Professor of Ore Dressing, Columbia University.

† Chemical Engineer.

M. L. Griffin.—That is what I would expect.

F. A. Jordan, Youngstown, Ohio.—Where did the author get the term "massive hematite"?

W. E. Keck.—It is used universally to designate material that has no macrocrystalline properties. It probably is unfortunate, but that was the sense in which it was used in this case.

I think there is some misunderstanding on the terms, solid and spongy hematite. The solid and spongy hematites were both massive hematite and they were separated by tabling. One was solid whereas the other had holes or voids like a sponge.

O. C. Shepard,* Stanford University, Calif. (written discussion).—What are others doing to compare results of flotation tests when both the recovery and grade of concentrate must be considered? Recently, I talked with a man who had completed 2500 flotation tests on the Flin Flon ore. A series of tests was made with each reagent, and the results were plotted on a graph with percentage of recovery as ordinate and grade of concentrate as abscissa. Generally, conditions that gave low-grade concentrate also gave a slightly lower recovery, and for each series of tests there was a point of maximum recovery and grade of concentrate. This maximum point was then compared with other series of tests, using different reagent combinations. Following the curve along toward higher grade concentrates, the recovery dropped off rapidly beyond the maximum point, as would be expected. The feature that I had not expected was that the recovery was generally lower than the maximum with conditions giving a low-grade concentrate.

Member.—Is any additional experimentation contemplated, to find the reasons why these addition agents function as they do?

W. E. Keck.—After the completion of this work, if it is thought that the problem is still worth while, we intend to continue. We have yet to report on the flotation of synthetic mixtures, one of the other phases of the problem, and also on ores. Before we go any further, we must complete these phases, and it all depends on whether the problem then is of interest.

O. Lee,† Birmingham, Ala.—What is the effect of pulp density on the flotation of hematites? In the beneficiation of Alabama red ores, fine grinding is likely to produce a considerable amount of what we call slime; in other words, minus 100-mesh material. In the normal course of gravity concentration, we cannot always control the pulp density of the slime. Assuming that flotation is applicable to the slimes, must there be a close control of the pulp density?

W. E. Keck.—Pulp density in all these tests was about 20 per cent solids. We did do some work with different pulp densities, and, I speak now from memory, I believe it did slightly increase the floatability of hematite. But there was no marked advantage. I think we carried it up to 30 per cent solids or thereabouts, and could not note any great advantage, possibly a slightly larger grain was floated.

O. Lee.—Where there is a certain amount of almost colloidal material, would the increase in pulp density tend to increase the recovery of that material?

---

* Associate Professor of Mining and Metallurgy, Stanford University.

† Republic Steel Corporation.

W. E. KECK.—I cannot say. We did some work on slimes in which we attempted to determine the effect of slimes designedly added. On coarse minus 65 plus 200-mesh hematite, we found that very small amounts (not enough to cause any appreciable change in pulp density) had a slight activating effect. Thereafter, larger quantities of the slime consumed the reagent and caused depression.

C. E. LOCKE,* Cambridge, Mass.—Is the author ready to predict as to the technical floatability of iron ore? I do not mean from the economic viewpoint, but merely as to whether a separation may be developed as possible. I say "iron ore" without regard to its form.

W. E. KECK.—We find that one of the first requisites for any separation is absence of slimes. Further, we find that we can make a fairly good separation on siliceous ores; that is, providing they are of reasonably coarse texture.

On the high-phosphorus ores, we have made some separation. The separation is not nearly as cleancut as in sulphide flotation, but probably it will compare favorably with nonmetallic separation.

C. E. LOCKE.—In other words, it is promising?

W. E. KECK.—Yes, there is some promise, and the same holds true of the high-sulphur ores. We have been able to make a certain amount of separation.

---

* Professor of Mining and Ore Dressing, Massachusetts Institute of Technology.

# A Study of the Flotative Properties of Magnetite

By W. E. Keck,* Associate Member A.I.M.E. and Paul Jasberg†

(New York Meeting, February, 1937)

The flotative properties of the principal minerals in Michigan's potential iron ores have been investigated to develop methods of beneficiation for the ores. One of these minerals, magnetite, is of considerable importance as a source of iron. Study of its flotation was similar to that of hematite[1], another iron mineral in these potential ores. The present research consisted essentially of: (1) a survey of the literature on magnetite flotation, (2) the preparation of pure magnetite, (3) the development of laboratory procedure and (4) flotation experimentation.

*Literature on Magnetite Flotation.*—For the purpose of this discussion, the results of previous work on the flotation of magnetite can be summarized as follows. The mineral has been floated with pine oil[2], and it has also been separated from synthetic mixtures with silicates by the use of the same reagent[2]. Magnetite and apatite in iron-ore slimes have been separated by flotation of apatite with sodium palmitate[3]. These data were utilized in the present investigation.

*Preparation of Magnetite.*—The pure mineral was prepared from the magnetic-separator concentrate of an iron ore (obtained from the Witherbee Sherman Corporation, Port Henry, N. Y.). This concentrate was slowly comminuted with laboratory rolls and pulverizer to pass 65-mesh and was then tabled several times. Tabling yielded a relatively coarse magnetite concentrate, tailing and slimes. The two latter materials were rejected insofar as the present work is concerned, and treatment of the magnetite (table concentrate) was continued by separating it into $-65 + 200$ and $-200$-mesh sizes. Separation of the sizes was made by first dry screening and then wet screening. The $-200$-mesh material was rejected to eliminate possible introduction of error into flotation

---

This paper describes a part of a general investigation into the flotation of Michigan's potential iron ores. A comprehensive discussion of the status of these ores and of the reasons for research on their flotation beneficiation is available in mimeographed form on application to the Michigan College of Mining and Technology, Houghton, Michigan. Manuscript received at the office of the Institute Nov. 12, 1936. Issued as T.P. 801 in Mining Technology, May, 1937.

* Research Engineer, Michigan College of Mining and Technology, Houghton, Mich.

† Laboratory Research Assistant, Michigan College of Mining and Technology.

[1] References are at the end of the paper.

results by the mechanical enmeshment of fine magnetite in the froth. Finally the −65 + 200-mesh magnetite was leached with distilled water to remove soluble impurities.*

The −65 + 200-mesh purified magnetite was analyzed to determine whether it was pure enough for the proposed research. When examined with a low-powered microscope, the material appeared to be composed almost entirely of magnetite, small quantities of quartz and iron silicates, and a trace of pyrite. Because quartz and the other impurities are insoluble under the usual flotation conditions, it was concluded that the presence of these quantities of impurities would not introduce a serious error in the flotation results.

A pulp was made of 50 grams of the magnetite and 200 c.c. of distilled water (pH of 6.1). The pH of the filtrate from this pulp was 6.8 to 6.9.

Chemical analyses of the magnetite, dried at 100° C., indicated that it contained the following quantities of materials: iron, 70.83 per cent; phosphorus, 0.020 per cent; silica, 0.54 per cent; manganese, 0.04 per cent; alumina, 0.06 per cent; lime, 0.48 per cent; magnesium oxide, 0.12 per cent and sulphur, 0.191 per cent. These quantities nearly equaled the theoretical ones for magnetite (72.40 per cent of iron and nothing of the other substances) and they indicated that approximately 97 per cent of the material was magnetite.

A study of all these analytical results led to the conclusion that the magnetite was pure enough for the proposed research; consequently, it was used for the present experimentation with the mineral. Sufficient quantities of the pure magnetite having been prepared, the flotative properties of the mineral were studied in the following manner.

*Flotation Procedure.*—The cell and flotation procedure have been previously described[4]; therefore only the following change from this procedure need be mentioned here. Froth was collected for 10 min. instead of 5 min., in order to make the results from magnetite comparable with those from hematite, which was also floated for 10 min. All of the flotation reagents were chemically pure except the following: technical ammonium laurate and sodium silicate; U.S.P. oleic acid; "neutral powder" sodium oleate; and sodium oleyl sulfate of unknown purity.

*Presentation and Discussion of Data.*—The presentation and discussion of data have also been previously described[4]; therefore this subject need not be discussed at this time.

*General Plan of Experimentation.*—The flotative properties of magnetite with soaps and fatty acids and under acidic and alkaline conditions were observed to be similar to those of the hematites under the same conditions. Therefore it was assumed that parallel tendencies would be also shown under other conditions, and the flotative properties of magnetite under the usual nonsulfide flotation conditions were not investigated as exhaustively as those of specular and massive hematite had been studied[1]. Instead, research was concentrated on an examination of the activation and depression with metal salts, for which magnetite seemed to be better suited than massive or specular hematite.

---

* It was assumed that sufficient leaching of the magnetite was reached when a negative qualitative test was obtained for the usual soluble impurities. A pulp of 50 grams of ore and 200 c.c. of distilled water was agitated in a flotation cell for 15 min. The filtrate from this pulp was then tested qualitatively for soluble material.

The present study of magnetite was principally concerned with the effect of various flotation reagents; therefore, in this article, the work is classified and discussed as far as possible from that standpoint.

## EXPERIMENTATION

*Fatty-acid Soaps and a Sulphated Alcohol.*—The data of Fig. 1 show: (1) that as collectors for magnetite, sodium oleate and "ammonium palmolate"* were markedly superior to ammonium laurate and sodium oleyl sulfate and (2) that the use of 0.10 lb. terpineol greatly increased flotation with sodium oleate. Sodium oleate having been determined a good collector for magnetite, the flotative properties of the mineral with this

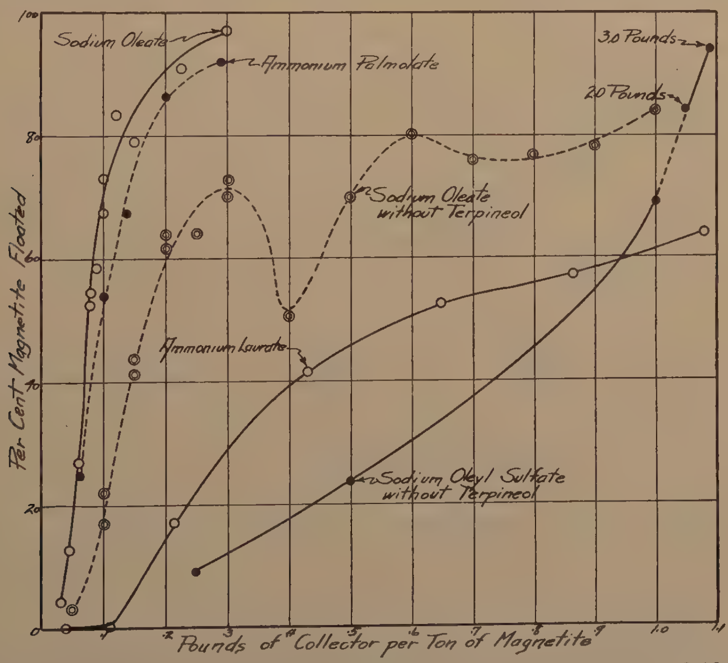


FIG. 1.—FLOTATION OF MAGNETITE WITH SEVERAL COLLECTORS AND 0.10 POUND TERPINEOL.

---

* An ammonium soap of palm oil.

reagent were compared with those of specular and massive hematites under similar conditions.

*Comparison of Flotation of Magnetite and Specular and Massive Hematites.*—To facilitate their comparison, the results from the flotation of these minerals with sodium oleate are shown in Fig. 2. The information on specular and massive hematites has been taken from previous work on these minerals[1]. In general, specular hematite was slightly more floatable than magnetite or massive hematite. However, this slight difference in floatabilities perhaps resulted from different distributions of grain sizes within the −65 and +200-mesh size limits of all three of the minerals.

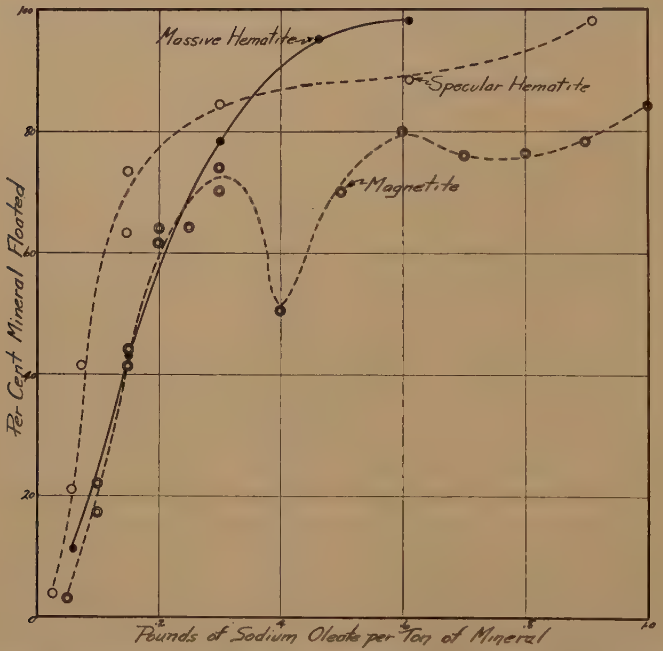


FIG. 2.—FLOTATION OF MAGNETITE AND MASSIVE AND SPECULAR HEMATITES WITH SODIUM OLEATE ONLY.

*Fatty Acids.*—The investigation was continued with a study of the fatty acids as collectors for magnetite. The data from these experiments (Figs. 3 and 4) show that flotation increased with the number of carbon atoms and that oleic acid was greatly superior to stearic acid.* This marked inferiority of stearic acid was due perhaps to its lack of dispersion in the pulp—the experiments having been conducted at room temperature. At this temperature, stearic acid is a solid but oleic acid is in the more dispersible liquid state.

---

* All of the fatty acids were added to the pulp in alcoholic solutions.

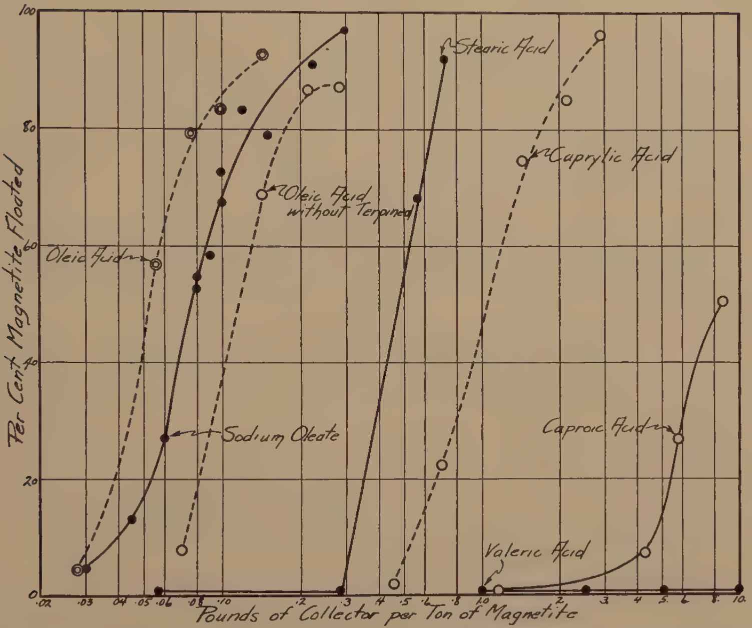


FIG. 3.—FLOTATION OF MAGNETITE WITH FATTY ACIDS AND 0.10 POUND TERPINEOL.

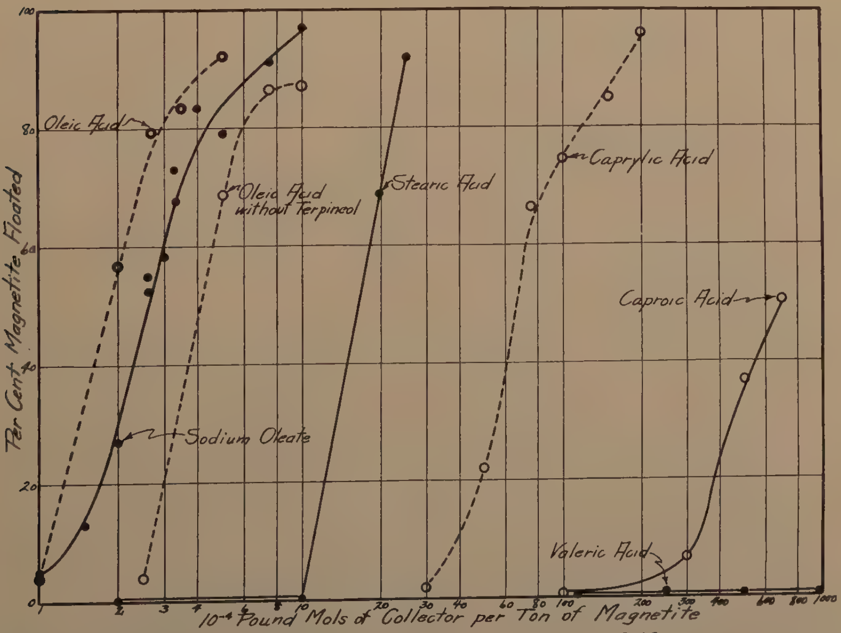


FIG. 4.—FLOTATION OF MAGNETITE WITH FATTY ACIDS AND 0.10 POUND TERPINEOL.

The addition of 0.10 lb. terpineol greatly increased the quantity of magnetite floated with oleic acid. A similar effect was observed when terpineol was used with sodium oleate for the flotation of magnetite. In both experiments, it was also observed that the froth was intensely flocculated without terpineol and that the addition of this reagent markedly improved the undesirable froth condition.

The data from sodium oleate have also been placed in Figs. 3 and 4, in order that the collective properties of this soap may be conveniently compared with those of oleic acid and the other fatty acids. Oleic acid was a stronger collector than sodium oleate but sodium oleate was more potent than any of the other fatty acids. Because the addition of oleic acid in alcoholic solution possibly introduced complications, experimentation was continued only with sodium oleate, which can be readily added in water solution.

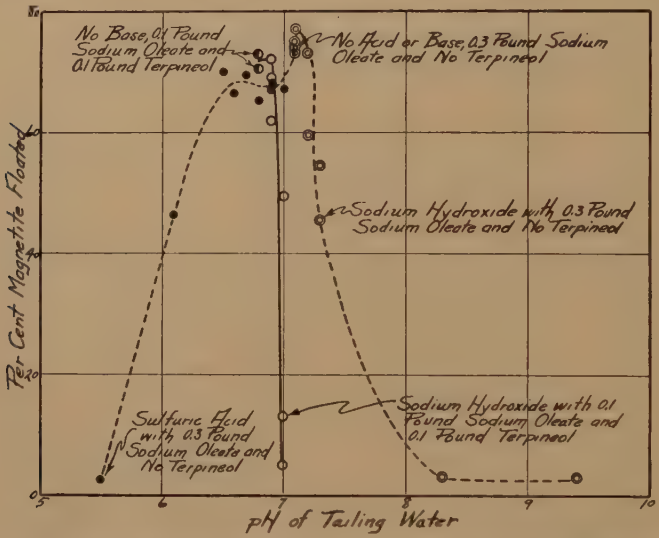


FIG. 5.—RELATION BETWEEN pH AND FLOATABILITY OF MAGNETITE.

*Sodium Oleate and Acidic or Basic Reagents.*—The results from these experiments are given in Figs. 5 and 7. To facilitate comparison of the flotation of magnetite and hematite under acidic and alkaline conditions, information from previous work on hematite[1] is shown in Figs. 6 and 7.

With decreasing pH, frothing was first slightly activated and then markedly depressed in the flotation of both magnetite and hematite. However, with increasing pH, frothing was markedly increased at all pH values with both magnetite and hematite—activation of frothing having been most pronounced in the experiments on massive hematite without terpineol.

The flotation of magnetite was more sensitive to changes in pH than the flotation of hematite. Practically no activation of magnetite was

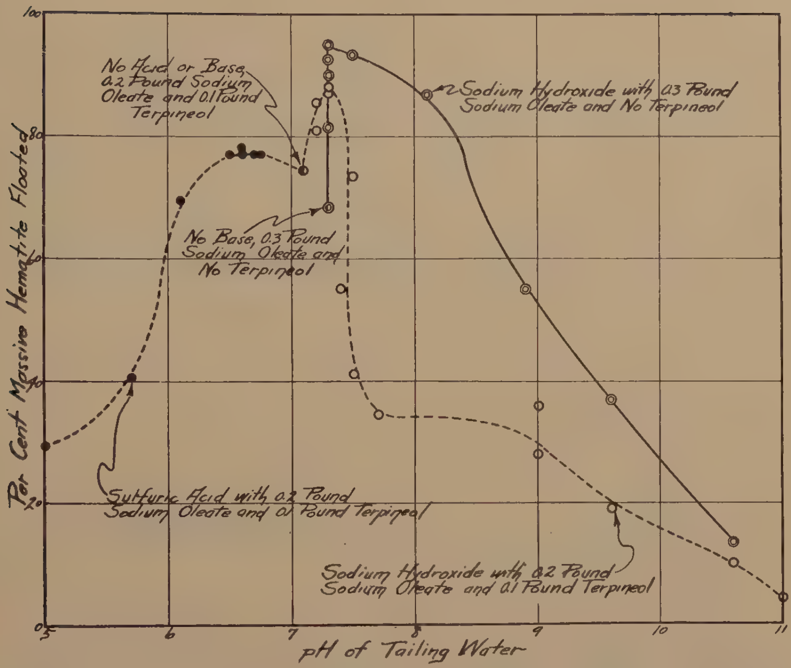


FIG. 6.—RELATION BETWEEN pH AND FLOATABILITY OF MASSIVE HEMATITE.

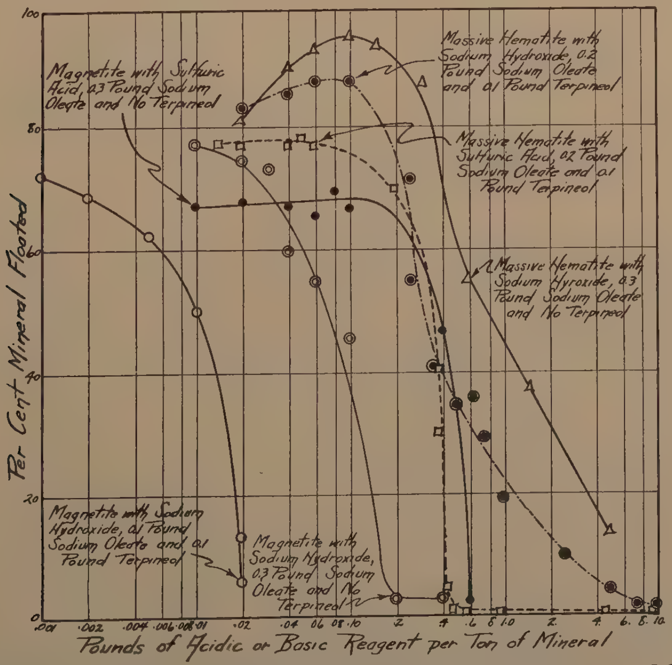


FIG. 7.—EFFECT OF SODIUM HYDROXIDE OR SULPHURIC ACID ON FLOTATION OF MAGNETITE AND HEMATITE WITH SODIUM OLEATE.

observed with small pH changes from neutral; but the flotation of massive hematite was considerably activated when the pH degree was increased and terpineol was absent. With slight alkalinity, activation of flotation was due perhaps to coincident increase in frothing. However, depression under more alkaline condition was not caused by a lack in quantity of froth, since the amount of water collected in the froth was always greater than at the neutral point. As an example, when the pH was 7.3, 68.5 per cent of the massive hematite was floated, and 58 grams of water were taken off in the froth; when the pH was 10.7, 8.5 per cent of the hematite was floated, and 168 grams of water were collected.

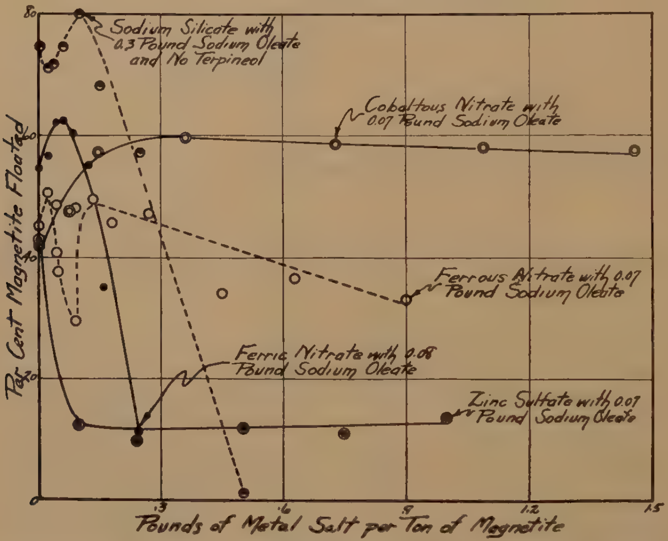


FIG. 8.—FLOTATION OF MAGNETITE WITH METAL SALTS, SODIUM OLEATE AND 0.10 POUND TERPINEOL.

The flotative properties of both magnetite and hematite under these conditions were, in general, similar, because relatively small pH changes from the neutral point markedly depressed both minerals. Since the flotative properties of magnetite and hematite were also similar in the other preceding experiments, further investigation was confined to the effect of metal salts with sodium oleate for the reasons discussed under General Plan of Experimentation.

*Sodium Oleate and Metal Salts.*—The quantities of magnetite floated with the sodium oleate-metal salt combinations are shown in Figs. 8, 9, 10 and 11, and the pH of the tailing waters from all of these experiments are given in Fig. 12. The data from sodium silicate have been included in these figures to conserve space.

The depression with sodium silicate was due perhaps to increase in pH. On the other hand, activation or depression or both were produced

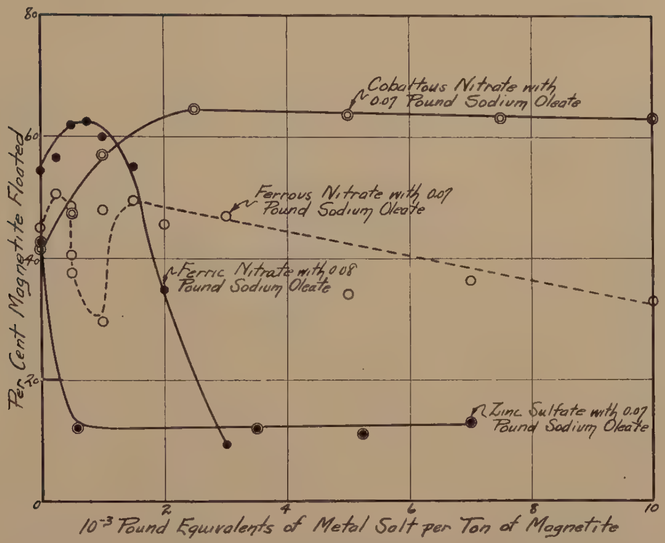


FIG. 9 —FLOTATION OF MAGNETITE WITH METAL SALTS, SODIUM OLEATE AND 0.10 POUND TERPINEOL.

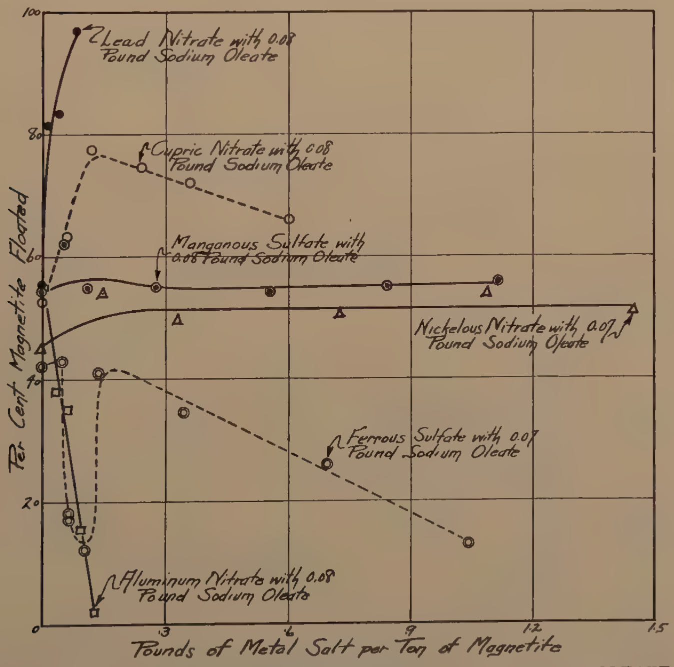


FIG. 10.—FLOTATION OF MAGNETITE WITH METAL SALTS, SODIUM OLEATE AND 0.10 POUND TERPINEOL.

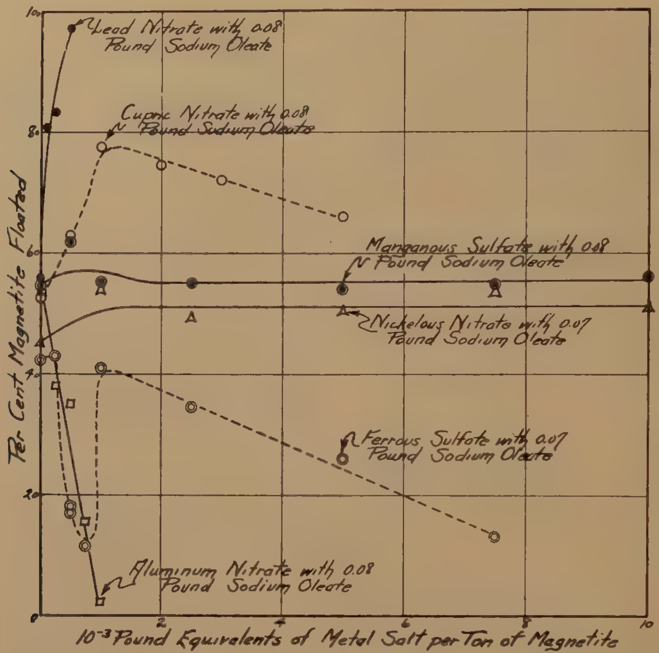


FIG. 11.—FLOTATION OF MAGNETITE WITH METAL SALTS, SODIUM OLEATE AND 0.10 POUND TERPINEOL.

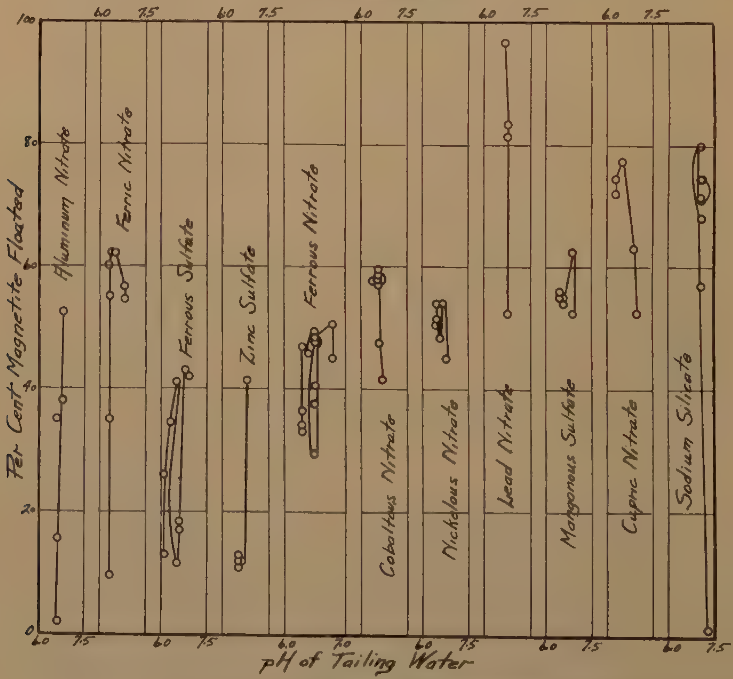


FIG. 12.—THE pH OF TAILING WATER FROM EXPERIMENTS SHOWN IN FIGS. 8, 9, 10, 11.

when the metal salts were used with sodium oleate. Thus the activation, at least, was caused by factors other than the slight decrease in pH which resulted from the addition of the metal salts.

Cobalt, manganese and nickel are closely related to iron. Small quantities of the salts from these metals activated the flotation of magnetite, but the addition of larger quantities of these salts produced no further change in flotation. These results are different from those with the other metal salts which produced either marked activation or depression, or both.

Because of the lack of solubility data on the metal soaps in question, the results obtained with the salts of the iron group, and also those obtained with other metal salts, cannot be discussed from the standpoint of solubility relations.

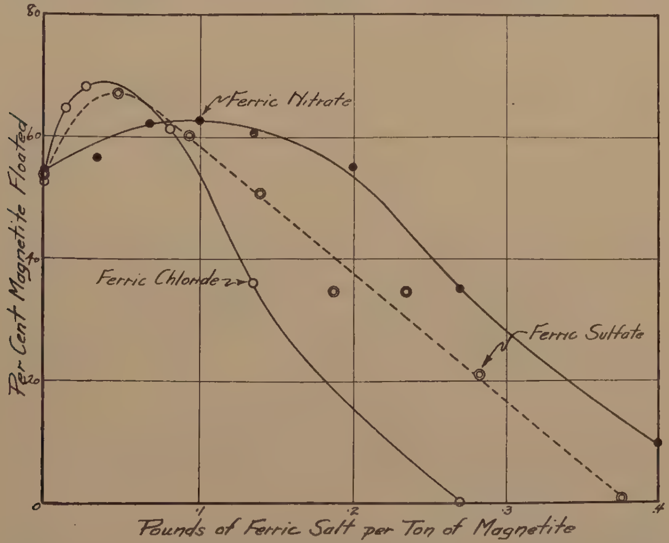


FIG. 13.—FLOTATION OF MAGNETITE WITH FERRIC SALTS. 0.08 POUND SODIUM OLEATE AND 0.10 POUND TERPINEOL.

The addition of increasing quantities of either ferrous sulphate or nitrate alternately activated and depressed flotation. The curves from these two ferrous salts are similar, but they are entirely different from the curve of ferric nitrate.

The ferric salts were studied and compared in the same manner as were the ferrous salts to determine whether the nature of the nonferric radical had any great effect on flotation. The data from this work are shown in Figs. 13 and 14. The results with the three ferric salts were similar—with increasing quantities of the salts, flotation was first slightly activated and then markedly depressed.

Ferric nitrate was further tested with ammonium laurate and ammonium linoleate. The quantities of magnetite floated with these reagents and with ferric nitrate and sodium oleate are shown in Fig. 15, and the pH values of the tailing solutions from the same experiments are given in Fig. 16. The results with the three collectors were similar; as before, flotation was first slightly activated and then greatly depressed with increasing quantities of ferric nitrate, activation and depression being most marked with ammonium linoleate.

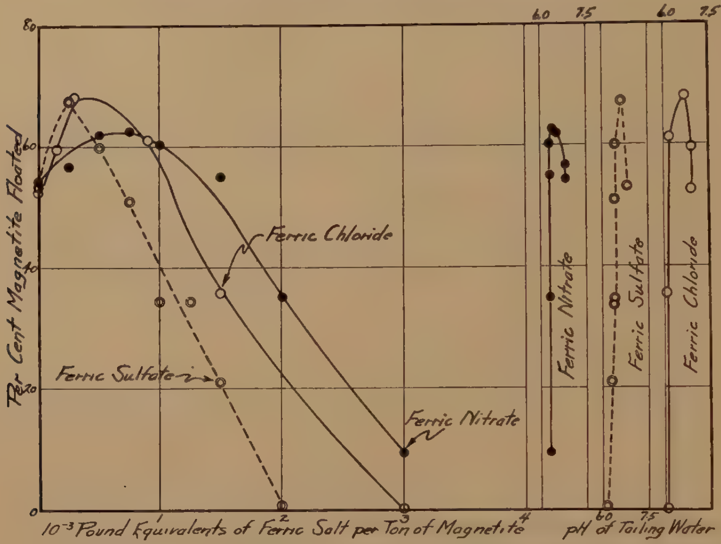


FIG. 14.—FLOTATION OF MAGNETITE AND pH OF TAILING WATER WITH FERRIC SALTS, 0.08 POUND SODIUM OLEATE AND 0.10 POUND TERPINEOL.

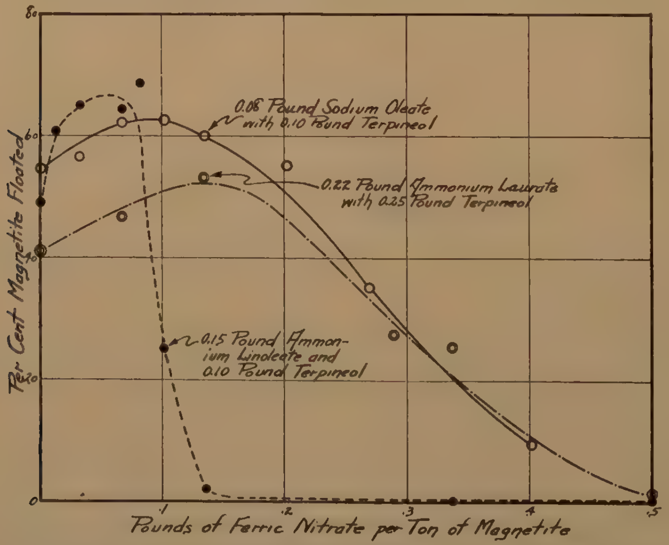


FIG. 15.—FLOTATION OF MAGNETITE WITH SEVERAL COLLECTORS, FERRIC NITRATE AND TERPINEOL.

*Sodium Oleate and Copper or Lead Nitrate.*—In preceding work with hematite[1], flotation was alternately activated and depressed with some metal salts. This phenomenon was also observed with magnetite when ferrous salts were used. The subject was further studied with magnetite because preliminary experiments indicated that this mineral is especially suitable for such work. This experimentation consisted essentially of flotation with different quantities (constant for each series) of sodium oleate and variable quantities of lead nitrate and copper nitrate. The results with lead nitrate are shown in Fig. 17, and those from copper nitrate are given in Fig. 18. The pH values of the tailing water from the experiments with both lead and copper nitrates are recorded in Fig. 16.

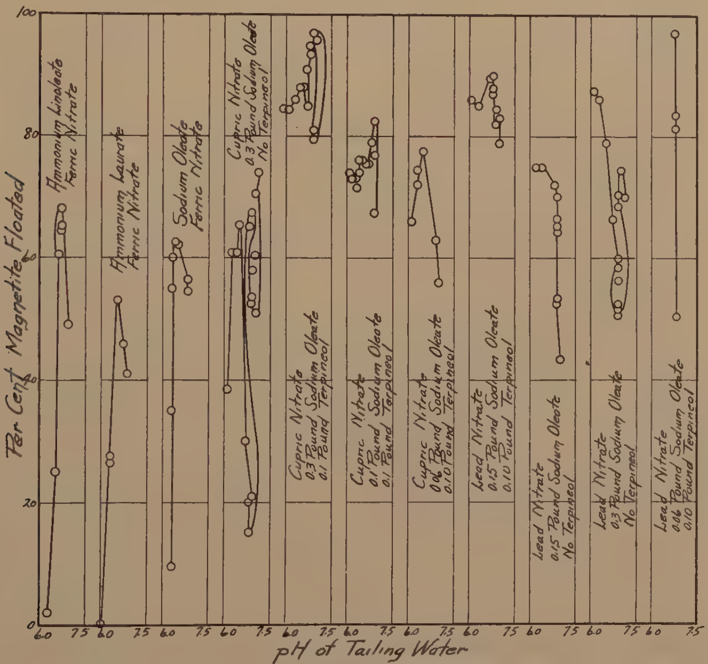


FIG. 16.—THE pH OF TAILING WATER FROM EXPERIMENTS SHOWN IN FIGS. 15, 17, 18.

Some of the curves of Fig. 16 show activation with decrease in pH; and others show both activation and depression. Thus the fundamental cause of activation and depression undoubtedly is not the decrease of pH that was brought about by the addition of the lead and copper nitrates.

In the experiments with the smaller quantities of sodium oleate, frothing was more affected than the amount of mineral that was floated. Addition of lead and copper nitrates produced activation throughout each series; but there were marked increases and decreases of the quantity of water in the froth and of the percentage of solids in the froth.

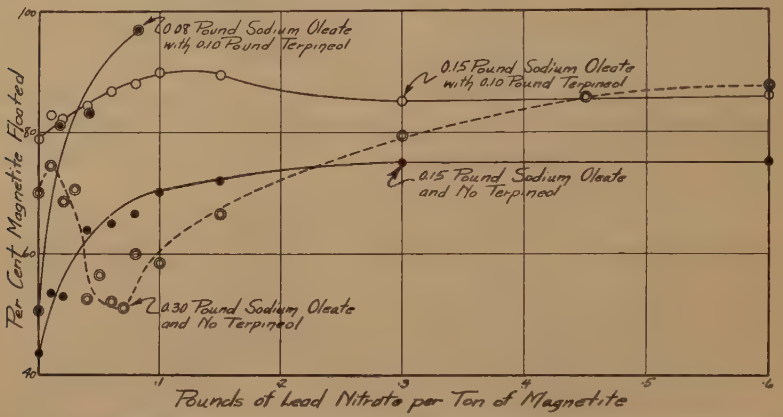


FIG. 17.—FLOTATION OF MAGNETITE WITH LEAD NITRATE AND SODIUM OLEATE.

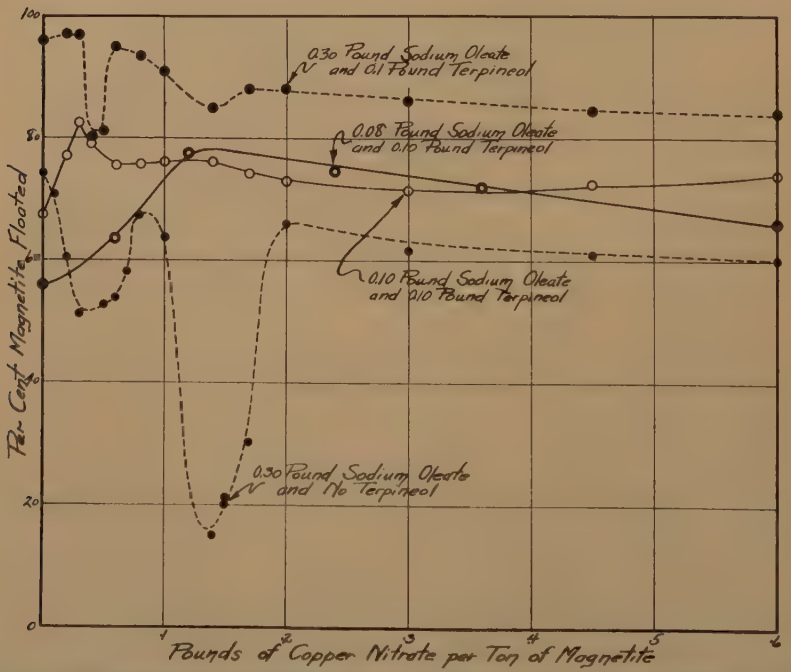


FIG. 18.—FLOTATION OF MAGNETITE WITH COPPER NITRATE AND SODIUM OLEATE.

Both activation and depression were observed with the largest quantity of sodium oleate (0.30 lb.). Activation of flotation occurred with an increase in the percentage of solids in the froth when terpineol was absent, and depression coincided with an increase in percentage of solids when terpineol was present in the system. A more comprehensive study of this subject is necessary to determine the causes of these phenomena.

With 0.15 lb. sodium oleate and no terpineol, flotation was first considerably activated and then remained constant with increasing quantities of lead nitrate. Under the same conditions with terpineol, the results were similar to the foregoing except that greater quantities of magnetite were floated and the flotation was slightly decreased with the larger quantities of the lead salt. However, flotation was markedly depressed and then activated again when 0.30 lb. of sodium oleate and no terpineol were used with increasing quantities of lead nitrate.

With copper nitrate, the results were approximately the same as with lead nitrate. When 0.06 and 0.10 lb. sodium oleate were used, activation was less and depression was more pronounced than with the lead salt. The use of a larger quantity of sodium oleate, 0.30 lb., with copper nitrate produced more marked activation and depression than it did with lead nitrate.

The addition of 0.10 lb. terpineol to copper nitrate and 0.30 lb. sodium oleate increased the quantity of magnetite that was floated, and also reduced the activation and depression. Preliminary experiments indicated that this activation and depression were also reduced, if not entirely prevented, by the addition of the sodium oleate and the metal salt in stoichiometric quantities. A continuous increase in flotation—from 4 to 98 per cent—was observed when increasing, chemically equivalent quantities of sodium oleate and lead nitrate were used in the experiments. The quantities of these reagents, varied by increments of 0.0001 lb. equivalent, ranged from 0.0001 to 0.001 lb. equivalent.

Activation and depression were absent with the smaller quantities of sodium oleate, but these variations in flotation were especially marked with 0.30 lb. of sodium oleate. This condition supports a hypothesis that has been previously advanced to explain the recurrent activation and depression of flotation[1]. In this hypothesis it was assumed that the phenomenon was due to the orientation of the adsorbed metal-soap molecules—the polar portions of successive layers of molecules being alternately orientated toward the mineral and away from it. When the smaller quantities of sodium oleate were used, not enough of collector was available to film the mineral with several layers of metal-soap molecules. Consequently, as increasing quantities of metal salts were added to the flotation system, activation was obtained but not subsequent depression and reactivation. However, as previously mentioned, before these facts can be more definitely established the relation between this phenomenon and frothing must be carefully studied.

The experiments with sodium oleate and copper and lead nitrates concluded this study of the flotative properties of magnetite. The information that was gained in this study has been applied in the flotation of potential iron-ore samples. The results of this work will be published in the near future.

## Summary and Conclusions

The flotative properties of magnetite were studied because this mineral is of considerable importance in the potential iron ores of Michigan. Relatively pure natural magnetite was used in these experiments, which were carried out under carefully controlled conditions.

Magnetite was readily floated with sodium oleate, ammonium laurate, and sodium oleyl sulphate. Sodium oleate was markedly superior to the other two collectors. The addition of terpineol, a frother, materially increased flotation with sodium oleate.

With the saturated fatty acids (valeric, caproic, caprylic and stearic acids), flotation increased with the number of carbon atoms. Unsaturated oleic acid with 18 carbon atoms was a better collector than saturated stearic acid, which also has 18 carbon atoms.

Flotation of magnetite with sodium oleate was greatly depressed by slight pH changes caused by the addition of sodium hydroxide or sulphuric acid.

In general, the flotative properties of magnetite were similar to those of hematite. Both minerals were readily floated by the usual fatty acids and their soaps. With sodium oleate, specular hematite was slightly more floatable than magnetite, and depression by an acid or a base was somewhat greater with magnetite than with hematite.

When it was used with sodium oleate, sodium silicate was a strong depressor for magnetite.

With small quantities of sodium oleate and terpineol, aluminum nitrate and zinc nitrate strongly depressed flotation and copper, and lead nitrates considerably activated it; whereas cobaltous, manganous and nickelous salts produced little change in flotation.

The use of ferric nitrate with sodium oleate first activated flotation and then nearly completely depressed it with increasing quantities of the ferric salt. Under the same conditions, ferrous nitrate produced two cycles of activation and depression. Similar results were obtained when the following substitutions were made: (1) ferrous sulphate for ferrous nitrate, (2) ferric chloride or sulphate instead of ferric nitrate and (3) ammonium laurate instead of sodium oleate.

The use of copper or lead nitrate with relatively large quantities of sodium oleate caused recurrent activation and depression of flotation. The presence of terpineol or of smaller quantities of sodium oleate tended to decrease this activation and depression.

## Acknowledgments

The authors gratefully acknowledge the aid they received in this work. They are especially indebted to G. C. Dillman, President, and N. H. Manderfield and C. T. Eddy, Associate Professors of Metallurgy, of the Michigan College of Mining and Technology, Houghton, Mich. The services of a laboratory assistant were provided under Project 31-F2-59 as a part of a cooperative research program sponsored by the Federal Emergency Relief Administration.

## REFERENCES

1. W. E. Keck, G. C. Eggleston and W. W. Lowry: A Study of the Flotative Properties of Hematite. Page 102, this volume.
2. C. G. McLachlan: Synthetic Testing for Flotation. *Bull.* Can. Inst. Min. and Met. (1926) **173,** 1013.
3. N. Luyken and E. Bierbrauer: Recovery of Apatite from Waste Ore Slimes by Flotation. *Mitt.* K. W. Inst. Eisenforsch., Dusseldorf (1928) **10,** 317–321.
4. W. E. Keck and P. Jasberg: A Study of the Flotative Properties of Gypsum. *Trans.* A.I.M.E. (1938) **129,** 218.

## DISCUSSION

[For discussion of this paper see page 125.]

# Flocculation and Clarification of Slimes with Organic Flocculants

By George R. Gardner,* Junior Member A.I.M.E., and Kenneth B. Ray†

(New York Meeting, February, 1939)

The application of wet cleaning processes for the beneficiation of bituminous coal has created in some localities a problem in the recovery and disposal of fine solids in the washery water. The maximum allowable concentration of these solids in the washery circuit that is consistent with satisfactory operation of the cleaning units remains a controversial point. It has, however, been generally recognized for a number of years that some degree of control should be exerted over the concentration of such material.

Early methods of control involved intermittent or continuous discharge of a portion of the plant slurry into near-by streams or settling ponds, and this persisted even after the adoption of settling tanks or cones. The practice is not always economical, for two reasons: first, because of the waste of coal, and, second, because it is sometimes difficult and expensive to obtain an adequate supply of water. The latter condition often is aggravated by chemical treatment of the make-up water that is necessary to prevent excessive corrosion of plant equipment. The modern approach to this problem has been the adoption of continuous thickening devices. However, because such equipment occupies considerable plant space and is somewhat expensive to construct, the practice of loading these thickeners beyond their rated capacity is widespread, therefore often the performance of such units is not altogether satisfactory.

In recent years, European washeries have increased the rate of settling of the fine coal from the slurry by the addition of specially prepared starch solutions. These reagents cause flocculation of the solid particles and thereby increase the rate of sedimentation.

The first important work on the flocculation and clarification of coal slurry was done by Henry, who developed the Henry process and used it successfully in Belgian preparation plants. Soon after the initiation in Belgium, the process was introduced into England, where subsequent investigation developed similar processes, which were successfully used in

---

Manuscript received at the office of the Institute Dec. 19, 1938. Issued as T.P. 1052, February, 1939. Also in Mining Technology, May, 1939.

* Sales Engineer, A. M. Meincke & Sons, Inc., Chicago, Ill. Formerly Chemist, Pittsburgh Coal Co.

† Research and Development Department, Mine Safety Appliances Co., Pittsburgh, Pa. Formerly Chemist, Pittsburgh Coal Co.

English plants. English investigators, including Raybould, Samuel, Wilkin, Needham, Holmes, and others, studied various phases of the problem.

In 1929, P. S. Gardner, Sr., of Koppers-Rheolaveur Co., who had seen the work in Belgium, suggested a plant test at Champion No. 1 Preparation Plant of the Pittsburgh Coal Co., using frozen starch and caustic. Immediately following this, P. S. Gardner, Jr., conducted tests on settling solids from washery water in a 12-ft. diameter settling cone at the Champion No. 1 plant. The results of the tests in which frozen starch was used were not wholly satisfactory, owing to difficulty in maintaining uniform flocculation. C. Q. Campbell, of Koppers-Rheolaveur Co., became interested in the possibilities of flocculation of coal slurry by means of starch treatment, and late in the year 1930 a full-scale plant test was made at Champion No. 1 plant using a reagent prepared by causticizing heated starch. The results of this test were reasonably satisfactory and showed clearly the possibilities of starch treatment for clarifying washery water.

In 1933 because of increased hourly tonnage, a higher percentage of fines in the raw coal, and a change in the characteristics of these fines, the problem of clarifying washery water became more serious than before. The Pittsburgh Coal Co. then started more laboratory and plant tests. S. B. Barley and William Robert tested a wide range of reagents, and starch was found to be one of the most effective in plant and laboratory tests.

While British and other European investigators have described and discussed the advantages of organic flocculants from an operating viewpoint, little attention has been given to the variables involved in the preparation of the starch reagent. This laboratory investigation into the preparation and properties of organic flocculating reagents was carried on by C. G. Black from February to July 1936, and by the authors from July 1936 to the middle of 1937.

There has been a twofold purpose in the present study: (1) to develop methods by which cheap materials could be used as flocculating reagents, and (2) to secure information on the flocculation process. A wide range of materials has been investigated and many of the variables that affect flocculation have been studied.

It has been found that the capacity of existing settling equipment can be markedly increased by the use of flocculating reagents, and their use is now a regular part of the plant operation.

## Experimental Methods

A review of the literature disclosed a number of methods for obtaining data relative to flocculation and sedimentation of the solids present in a coal slurry. Most previous work has been conducted in glass cylinders or similar types of vessels. With this type of container it is often difficult to observe the line of demarcation of the solids as settling occurs. Some investigators have found it necessary to measure changes in the concentration of solids due to sedimentation by withdrawing small volumes of the slurry as settling proceeded. Such a practice is obviously cumbersome and lengthy. To obviate these difficulties, a modification of the Henry settling frame was adopted for this investigation.

The settling frame consists of two glass plates, 7 by 19 in., held about ¼ in. apart by means of a rubber hose threaded with soft soldering wire. The plates are held in position by two wooden frames, connected by stove bolts ¼ in. in diameter. The distance between the glass plates is adjusted so that a volume of 500 ml. of slurry occupies a height of about 40 cm. The frame is lighted from the rear, with a reflector covered with a frosted glass plate, and a centimeter scale is fastened to the front glass of the frame.

The following procedure was followed in all tests: A 25-gram sample of dry solids was mixed with 100 ml. of water and allowed to stand overnight to insure thorough wetting of all particles. The sample was diluted to 500 ml. and the temperature adjusted to 29° C. The flocculating reagent was added and the sample poured back and forth between two beakers six times. It was then poured into the settling frame through a flat funnel. The time in seconds for each 4-cm. drop of the dividing line between solid and liquid was recorded until the zone of compression was reached. During the test the light was placed about one foot to the rear of the frame and the eyes of the observer were kept on a level with the line of demarcation of the solids.

## METHOD OF RECORDING DATA

It has been found convenient to express the results of a test in the settling frame by means of the "settling index"; that is, the number of seconds required for the solids to settle a distance of one centimeter in the zone of free settling. For a given slurry it is a measure of the degree of flocculation of the particles. The lower the index, the greater the rate of sedimentation and the degree of coagulation. No difficulty will be experienced if the reciprocal relationship between rate of sedimentation and the settling index is kept in mind.

TABLE 1.—*Comparison of Settling Index with Clarification Produced*

SLURRY, 5 PER CENT SOLIDS

| SETTLING INDEX, SEC. PER CM. | CLARIFICATION |
|---|---|
| 21 or greater | Very poor |
| 11 to 20 incl. | Poor |
| 6 to 10 incl. | Fair |
| 5 | Good |
| 4 or less | Very good (practically complete) |

Table 1 shows the general relationship that has been observed between the "settling index" and degree of clarification with a slurry containing

5 per cent solids. This relationship does not necessarily hold true for slurries having a higher percentage of solids.

In the procedure described for determining the "settling index," it is possible to duplicate the results to within 10 per cent.

In order to facilitate examination of tabulated data, the treatment used in many tests has been reported on a dry basis both as parts per million and as pounds of reagent per ton of solids. To convert from pounds per ton of solids to parts per million, multiply by five times the percentage of solids.

### ANALYSES OF SOLIDS AND WATER USED IN THIS INVESTIGATION

Solids used in preparing standard laboratory slurries were obtained by filtration of the feed to a continuous thickener at the Champion No. 1 preparation plant. Tables 2 and 3 show the analyses of the solids and water used in preparing laboratory slurries. Table 2 shows that 64.6 per cent of these dried solids pass a 200-mesh screen, while 82 per cent pass a 100-mesh screen.

These solids constitute but one-third of the total solids in the washery slurry but are the most difficult portion to settle. A large volume of slurry is fed into a continuous thickener 60 ft. in diameter, and a classification of the solids occurs. The underflow contains the larger coal particles and to a certain extent the fine pyrite, and the overflow contains a high percentage of minus 200-mesh material, including most of the clay. Two-thirds of the total solids is settled in the 60-ft. thickener. Part of the 60-ft. thickener overflow and all of the refuse boot overflow form the feed to the 85-ft. diameter thickener and the solids from this product were used in the investigation. An untreated slurry of these solids has a "settling index" of 65.

TABLE 2.—*Analysis of Solids from Continuous Thickener Feed*

| Size | Per Cent | Ash | Sulphur | Specific Gravity |
|---|---|---|---|---|
| Head | 100.0 | 28.6 | 3.2 | 1.60 |
| +28 mesh | 0.8 | 29.9 | 3.4 | 1.73 |
| 28–48 | 3.2 | 16.0 | 2.6 | 1.49 |
| 48–60 | 2.5 | 10.3 | 2.0 | 1.37 |
| 60–100 | 11.5 | 18.8 | 2.4 | 1.46 |
| 100–200 | 17.4 | 25.6 | 3.1 | 1.46 |
| −200 mesh | 64.6 | 32.8 | 3.4 | 1.66 |

It is of interest to note in Table 3 the marked increase in the mineral content of the plant slurry filtrate over that of the make-up water. It should be emphasized that there was practically no waste of water from the plant at the time these samples were taken. All filtrate water was being recirculated, and only sufficient make-up water was added to compensate for normal losses due to water carried out on the coal and refuse and to heat-drying losses.

TABLE 3.—*Comparison of Analysis of Water Used in Preparation of Laboratory Slurries with Plant Slurry Filtrate*

| | Make-up Water | Plant Slurry Filtrate |
|---|---|---|
| pH (potentiometric) | 7.2 | 8.3 |
| Titrated alkalinity (methyl orange), p.p.m. $Na_2CO_3$ | 159.0 | 170.0 |
| Mineral content, p.p.m.: | | |
| $SiO_2$ | 0 | 0 |
| $Al_2O_3$-$Fe_2O_3$ | 2 | 7 |
| CaO | 47 | 259 |
| MgO | 14 | 46 |
| $SO_4^{=}$ | 58 | 710 |
| $Cl^-$ | 7 | 493 |

## EFFECT OF PERCENTAGE OF SOLIDS ON SETTLING INDEX AS DETERMINED IN SETTLING FRAME

As the percentage of solids in the slurry increases, the rate of settling decreases. This effect is independent of the material or the treatment used. It is possible by a few tests to determine for any given material and treatment the percentage of solids that will give the best settling.

TABLE 4.—*Effect of Percentage of Solids on Settling Index and on Point of Compression in Settling Frame*

SLURRY TEMPERATURE, 29° C.

| Centimeters | Settling Index, Sec. per Cm. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Untreated Slurry | | | | Treated Slurry[a] | | | |
| | 5 Per Cent Solids | | 10 Per Cent Solids | | 5 Per Cent Solids | | 10 Per Cent Solids | |
| | 4-cm. Drop | Cum. | 4-cm. Drop | Cum. | 4-cm. Drop | Cum. | 4-cm. Drop | Cum. |
| 0–4 | 75 | 75 | 111 | 111 | 7 | 7 | 28 | 28 |
| 5–8 | 60 | 68 | 80 | 95 | 6 | 6 | 23 | 25 |
| 9–12 | 59 | 65 | 85 | 92 | 6 | 6 | 25 | 25 |
| 13–16 | 55 | 62 | 100 | 94 | 6 | 6 | 30 | 26 |
| 17–20 | 60 | 62 | | | 7 | 6 | 56 | 32 |
| 21–24 | 63 | 62 | | | 10 | 7 | | |
| Point of compression | 24 cm. | | 12 cm. | | 20 cm. | | 12 cm. | |

[a] 0.5 lb. starch causticized with 0.25 lb. caustic per ton solids.

Table 4 shows the effect of increasing the solids from 5 to 10 per cent for both untreated and treated samples.

With a slurry treatment of 0.5 lb. starch and 0.25 lb. caustic per ton of solids, it was necessary to keep the solids down to 5 per cent in order to secure a "settling index" below 10. With slurries of gold ore, it is possible to get excellent results with solids as high as 10 per cent. It appears that the maximum percentage of solids consistent with good operating results depends on the material. The higher the percentage of solids, the shorter is the zone of free settling and in general the better the degree of clarification.

In the following laboratory tests, the percentage of solids was maintained at 5, since in our application to clarification of coal slurries the feed to continuous thickeners is held near 5 per cent solids by using flocculating reagents. Before the use of flocculating reagents the slurry contained as much as 20 per cent solids in the latter part of the week.

## EFFECT OF TEMPERATURE ON SETTLING INDEX OF UNTREATED SLURRY

The effect of temperature of the slurry on the rate of settling is marked. Table 5 shows the variation of "settling index" with temperature on untreated slurry, but the same variation also holds for treated slurries. For this slurry the rate of settling increases four times in the range from 4° to 40° C. The results are not important practically above 30°, but the rapid decrease in the rate of settling at low temperatures has a direct application in cold weather.

TABLE 5.—*Effect of Temperature on Settling Index of Untreated Slurry Containing* 5 *Per Cent Solids*

| Temperature of Slurry, Deg. C. | Settling Index, Sec. per Cm. | Temperature of Slurry, Deg. C. | Settling Index, Sec. per Cm. |
|---|---|---|---|
| 4 | 146 | 25 | 68 |
| 10 | 81 | 29 | 63 |
| 15 | 82 | 35 | 43 |
| 20 | 78 | 40 | 37 |

## EFFECT OF pH OF SLURRY ON SETTLING INDEX

The effect of the pH on the rate of settling of solids from a slurry has been well established by other investigators and has been verified in this investigation. Table 6 shows that the minimum rate of settling is observed at a pH of 7.0 and that on either side of this neutral point the rate increases with the most pronounced rise on the alkaline side.

## MATERIALS INVESTIGATED AS FLOCCULATING AGENTS

At the outset of this investigation, a general study was undertaken of available materials that might be utilized as flocculating agents.

Twenty-five different raw materials were studied, of which 17 of the more interesting are summarized in Table 7, including substances containing starch, protein and cellulose. It was readily apparent that all of these could be used with some degree of success as flocculating agents. Attention need not be confined to starch only in consideration of a suitable material for a flocculating agent. Recent work with proteins and soluble forms of starch has shown clearly that these two general groups of substances can, with proper treatment, produce excellent results. Since starch offers a very attractive possibility as a general flocculating agent and is readily available at a reasonable cost, it is felt advisable to confine the present discussion to the preparation of reagents from this material.

TABLE 6.—*Effect of pH of Slurry on Settling Index*
5.0 PER CENT SOLIDS

| pH of Slurry | Settling Index, Sec. per Cm. | pH of Slurry | Settling Index, Sec. per Cm. |
|---|---|---|---|
| Less than 3.0 | 16 | 6.4 | 49 |
| Less than 3.0 | 21 | 6.5 | 53 |
| Less than 3.0 | 27 | 6.6 | 56 |
| 4.9 | 35 | 7.2 | 62 |
| 6.2 | 43 | 10.4 | 50 |
| 6.3 | 45 | 10.5 | 12 |

TABLE 7.—*Summary of Material Investigated as Flocculating Agents*[a]

| Reagent | Settling Index, Sec. per Cm. | Reagent | Settling Index, Sec. per Cm. |
|---|---|---|---|
| Starch "A" | 6 | Gluten | 6 |
| Crude potato starch | 5 | Zein | 11 |
| Refined potato starch | 5 | Pearl starch "C" | 6 |
| Soy bean flour | 6 | Starch "B" | 7 |
| Soy bean meal | 7 | Powdered starch "D" | 6 |
| Wheat bran | 6 | Beef extract | 8 |
| Distillery waste | 8 | Tapioca flour | 6 |
| Crude cornstarch | 6 | Oak sawdust | 14 |
| | | Wheat straw | 16 |

[a] 5 per cent solids. Slurry temperature 29° C. Treatment: 0.5 lb. starch causticized with 1.25 per cent NaOH at 100° C. Settling index of untreated slurry, 65 sec. per cm.

## METHOD OF PREPARING REAGENTS

The starch reagents were prepared by two methods, causticizing and heating. In causticizing, sufficient water was added to the starch to form a thin paste and caustic solution was added at the desired concentration and temperature. The resultant gel was adequately stirred and then diluted to a convenient concentration. Since gels containing a higher concentration of starch were difficult to dilute, starch was generally causticized at 5 per cent concentration.

Heat-treated starch solutions prepared below 100° C. were obtained by pouring water heated slightly above the desired temperature into the starch paste. The temperature immediately after addition to the starch paste was taken as the final temperature of preparation. In treatment involving temperatures in excess of 100° C., the starch paste was formed, diluted to 5 per cent concentration, and the whole was introduced into an autoclave and heated to the desired temperature. In order to facilitate the addition of small amounts of reagent, it was necessary to use solutions diluted to 0.5 per cent starch. It has been found, however, that the reagent may be used at concentrations up to and including 2.5 per cent starch without any substantial decrease in flocculating power. In most cases, the use of reagents containing more than 2.5 per cent starch is impractical because of the difficulty of regulating the rate of addition to the requirements of the plant circuit.

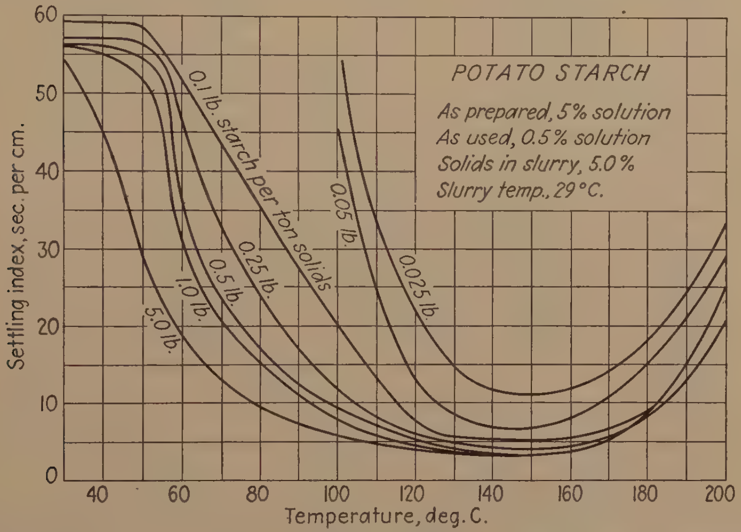


Fig. 1.—Effect of preparation temperature on flocculating properties of starch solutions.

## Variables Involved in Preparation of Flocculating Reagents from Starch

Any form of starch treatment that will produce flocculating properties results in the formation of a colloidal solution of at least a portion of the starch. The properties of such solutions are, as a rule, extremely sensitive to the conditions involved in their formation. The following conditions were found to be important: (1) temperature of preparation of starch solution, (2) concentration of caustic, (3) time of treatment, (4) degree of agitation during treatment, (5) age of reagent.

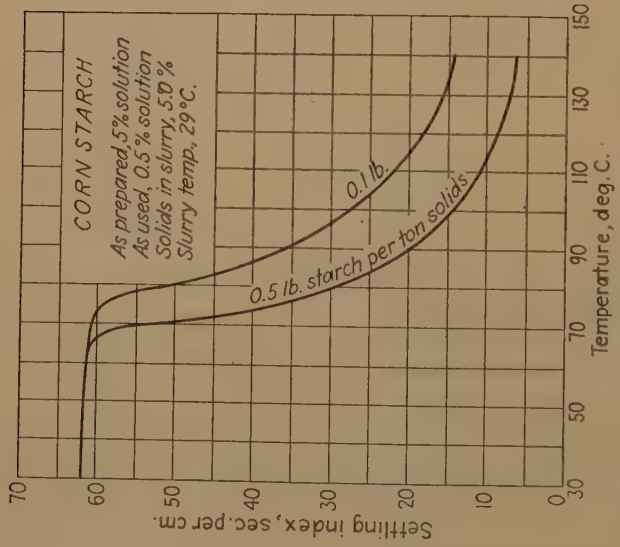


FIG. 2.

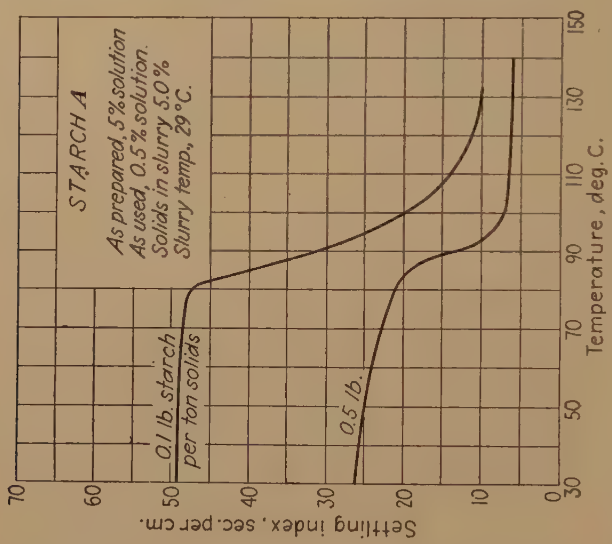


FIG. 3.

FIGS. 2 AND 3.—EFFECT OF PREPARATION TEMPERATURE ON FLOCCULATING PROPERTIES OF STARCH SOLUTIONS.

### TEMPERATURE OF PREPARATION OF STARCH SOLUTION

The importance of temperature in preparation of flocculating reagents from starch cannot be overemphasized. Heating under pressure in the range of 100° to 160° C. will convert starch into a reagent that is as efficient as the product of any form of treatment. The graphs of Figs. 1

to 3 show the change in flocculating properties with temperature for starch from several sources. Examination of a number of starches has shown that these data are, in a general way, applicable to all starches. As the temperature of an aqueous starch paste is raised, the starch grains expand. At temperatures ranging from 55° to 75° C., the starch grains rupture and the soluble portion of the starch is released. Figs. 1 to 3 show clearly that the solution acquires flocculating properties in this temperature range. Only a portion of the starch, however, has been

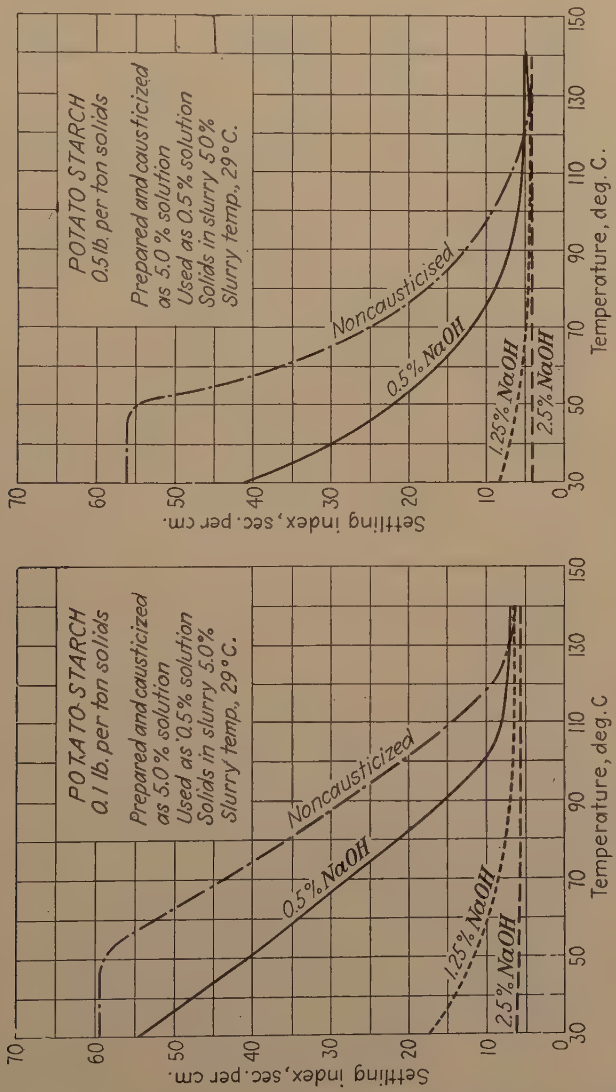


FIG. 5.

FIG. 4.

FIGS. 4 AND 5.—EFFECT OF PREPARATION TEMPERATURE AND STRENGTH OF CAUSTIC ON FLOCCULATING PROPERTIES OF POTATO STARCH SOLUTIONS.

dispersed at this point and in consequence the solution has not reached its maximum effectiveness. Further increasing the solution temperature above the point at which grain rupture occurs results in a progressive dispersion of this insoluble material and a consequent progressive increase in the effectiveness of the reagent. At a temperature of approximately 145° C. a starch solution acquires its maximum flocculating power and heating to higher temperature decreases the effectiveness of the starch as a flocculant.

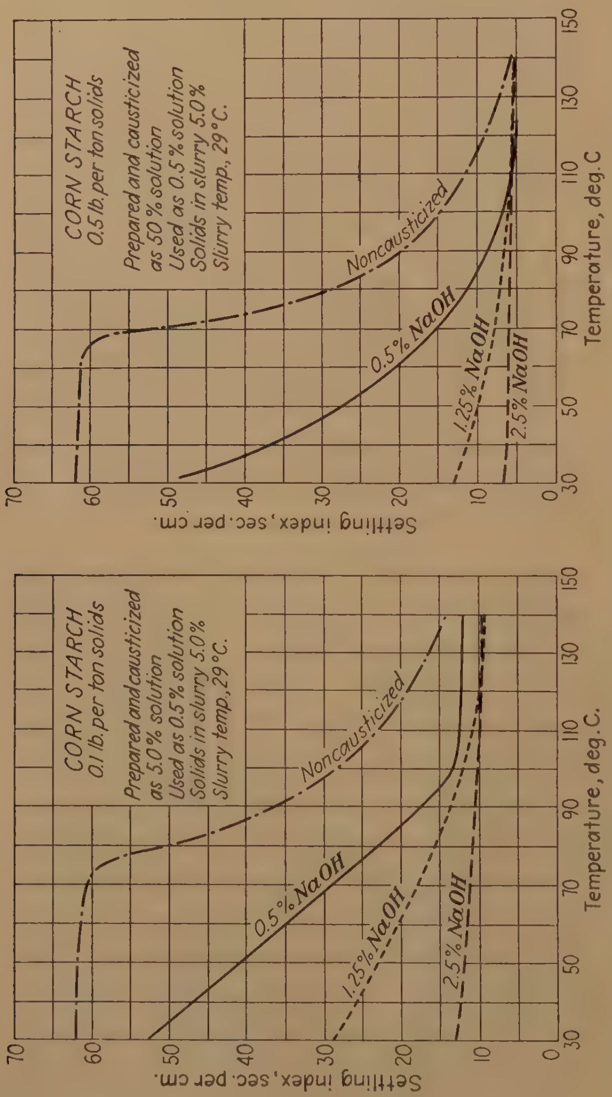


Fig. 7.

Fig. 6.

Figs. 6 and 7.—Effect of preparation temperature and strength of caustic on flocculating properties of cornstarch solutions.

## CONCENTRATION OF CAUSTIC

The term "causticized starch" implies that the starch has been treated with a solution of a caustic reagent. It has been shown previously that the temperature is an important factor in the preparation of noncausticized solutions. For causticized solutions, two factors must be considered concurrently, temperature and concentration of caustic. Efficient flocculating reagents may be produced at 25° C. by treating the starch with a 2.5 per cent solution of caustic soda. As the strength of caustic

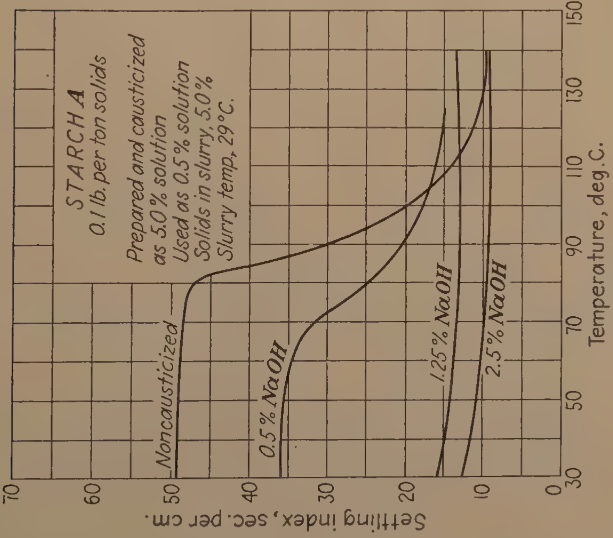


FIG. 8.

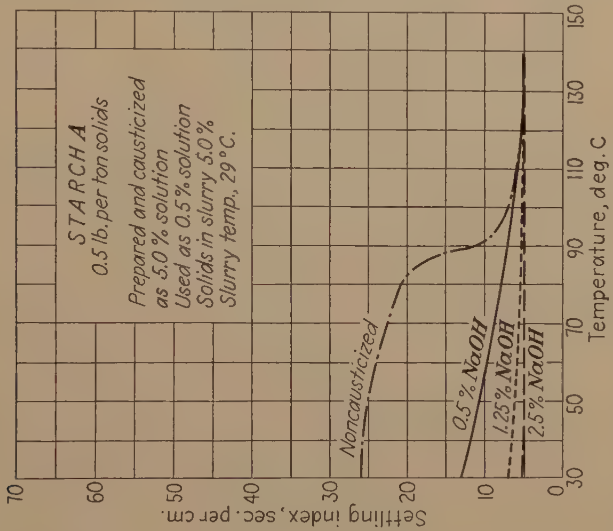


FIG. 9.

FIGS. 8 AND 9.—EFFECT OF PREPARATION TEMPERATURE AND STRENGTH OF CAUSTIC ON FLOCCULATING PROPERTIES OF STARCH A SOLUTIONS is progressively decreased, it is necessary to increase the temperature in order to produce an equally efficient reagent. Figs. 4 to 9 illustrate this point. The preparation of noncausticized starch reagents at temperatures of 140° to 150° C. (Figs. 1 to 3) produces about the same results as the use of a 2.5 per cent caustic solution at 25° C.

It is important to note that the chief advantage of maintaining optimum conditions in preparation of starch reagents lies in greater efficiency of the reagent. Improperly prepared solutions may produce flocculation if used in sufficiently large quantities, but observations of proper conditions in the preparation of the starch solution make it possible to attain the best results with a minimum amount of starch. Table 8 illustrates the remarkable increase in effectiveness of heat-treated starch solutions with increasing temperatures. An increase of 67° C. in the preparation temperature of the starch solution has decreased by two hundredfold the amount of starch treatment necessary to attain a "settling index" of 10 with this slurry.

TABLE 8.—*Effect of Temperature on Amount of Reagent Necessary to Attain Equivalent Rates of Settling*[a]

| Starch, Lb. per Ton Solids[b] | Temperature of Starch Solution, Deg. C. | Settling Index, Sec. per Cm. |
|---|---|---|
| 5.0 | 78 | 10 |
| 1.0 | 92 | 10 |
| 0.5 | 97 | 10 |
| 0.25 | 106 | 10 |
| 0.10 | 117 | 10 |
| 0.05 | 125 | 10 |
| 0.025 | 145 | 10 |

[a] 5 per cent solids treated with 0.5 per cent potato starch solution. Slurry temperature 29° C.

[b] To convert to parts per million, multiply by 25.

## TIME OF TREATMENT

In converting starch to the "soluble form" the treatment must be prolonged for a short period of time in order to obtain the best results. Tables 9 and 10 show the effect of time of heating on the flocculating power of starch reagents. It is apparent that prolonged heating of potato starch below the rupturing temperature has no effect on the starch but that prolonged heating at or above this temperature increases the effectiveness of the starch appreciably. Owing to the time required to cool and dismantle the autoclave, it was impossible to obtain periods of heating of less than 15 min. above 100° C. No improvement was observed when solutions were treated in the autoclave for more than

15 min. In general, 15-min. treatment is to be recommended for both causticized and heat-treated starch solutions.

Table 9.—*Effect of Temperature and Time of Heating on Flocculating Properties of Starch Solutions*

| Preparation Temperature of Reagent, Deg. C. | Settling Index, Sec. per Cm. | | | | |
|---|---|---|---|---|---|
| | Potato Starch | | | Starch A | |
| | Time of Heating | | | Time of Heating | |
| | 0.05 Min. | 15 Min. | 30 Min. | 0.05 Min. | 15 Min. |
| 40 | 60 | 60 | | 31 | 20 |
| 50 | 60 | 60 | | 28 | 21 |
| 60 | 60 | 24 | | 27 | 20 |
| 70 | 37 | 17 | | 23 | 21 |
| 80 | 23 | 12 | 11 | 19 | 9 |
| 90 | 19 | 8 | | 14 | 7 |
| 100 | 12 | 6 | 6 | 10 | 6 |

Table 10.—*Effect of Time of Heating on Flocculating Properties of Potato Starch Solutions*[a]

| Time Heating 80° C., Min. | Settling Index, Sec. per Cm. | Time Heating 80° C., Min. | Settling Index, Sec. per Cm. |
|---|---|---|---|
| 0.05 | 23 | 5.0 | 13 |
| 0.5 | 18 | 10.0 | 13 |
| 1.0 | 17 | 15.0 | 12 |
| 2.0 | 15 | 30.0 | 11 |
| 3.0 | 14 | 45.0 | 11 |
| 4.0 | 13 | 60.0 | 11 |

[a] 0.5 per cent starch solution. 0.5 lb. per ton solids. To convert to parts per million multiply by 25. 5 per cent solids. Slurry temperature, 29° C.

## Degree of Agitation during Treatment

Treating a 5 per cent starch paste with a solution of caustic soda yields a thick, viscous gel. It is not sufficient to form this gel and dilute it to the desired concentration; the gel must be thoroughly agitated to produce the best results. Fig. 10 shows the effect of stirring and time of causticizing on the flocculating properties of potato starch. During agitation there is a marked decrease in the rigidity of the gel and when sufficiently agitated the whole is fluid enough to pour freely.

It has been found that a solution of starch should not be treated either by heat or caustic at concentrations in excess of 5 per cent starch. The difficulty in using stronger solutions is that the gel that is formed cannot readily be dissolved or diluted. Causticizing starch solutions of less than 5 per cent starch gives as good results as are obtained by causticizing at 5 per cent and diluting. However, it is cheaper to treat in concentrated solutions, for less heat and caustic are required. Table 11 shows the effect of causticizing in dilute and concentrated starch solutions.

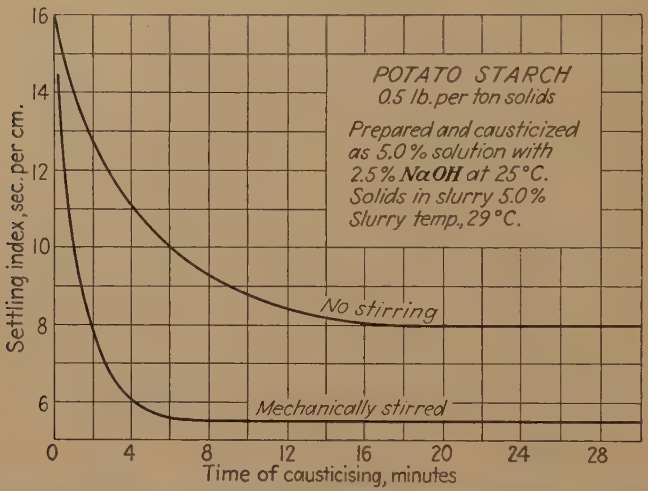


FIG. 10.—EFFECT OF TIME OF STIRRING AND TIME OF CAUSTICIZING ON FLOCCULATING PROPERTIES OF POTATO STARCH.

TABLE 11.—*Comparison of Causticizing Crude Potato Starch, Crude Cornstarch, and Starch "A" in Dilute and Concentrated Solutions*[a]

| Causticizing Temperature, Deg. C. | Settling Index, Sec. per Cm. | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Potato Starch | | | | Starch A | | | | Cornstarch | | | |
| | 0.1 Lb. per Ton[b] | | 0.5 Lb. per Ton[b] | | 0.1 Lb. per Ton[b] | | 0.5 Lb. per Ton[b] | | 0.1 Lb. per Ton[b] | | 0.5 Lb. per Ton[b] | |
| | D | C | D | C | D | C | D | C | D | C | D | C |
| 30 | 14 | 17 | 6 | 8 | 16 | 15 | 6 | 7 | 17 | 18 | 11 | 13 |
| 90 | 8 | 8 | 5 | 5 | 13 | 15 | 6 | 6 | 14 | 19 | 7 | 9 |
| 100 | 7 | 6 | 5 | 5 | 10 | 12 | 6 | 6 | 10 | 12 | 5 | 6 |
| 140 | 6 | 6 | 6 | 5 | 15 | 17 | 8 | 6 | 9 | 8 | 6 | 6 |

[a] 5 per cent solids. Causticizing solution 1.25 per cent NaOH. Slurry temperature 29° C. C indicates causticized 5 per cent starch, etc.; D, causticized 0.5 per cent starch, etc.

[b] To convert to parts per million multiply by 25.

## Age of Reagent

From a practical point of view, it is extremely important to know how long these flocculating agents will retain their properties. Starch A, prepared by heat-treatment only, deteriorated more rapidly than any other reagent, and after a few days in storage had a dispersing rather than a flocculating action. Other heat-treated starches retained their flocculating properties up to and including three days. Causticized starches retained their flocculating properties for a much longer period of time than did heat-treated starch solutions. Some causticized solutions set for nearly two weeks have shown no appreciable deterioration. The deterioration of these settling reagents is apparently a form of bacteriological fermentation; hence it is reasonable to assume that the reagents would exhibit the properties mentioned above. Starch A contains dextrinized starch, which is readily attacked by bacteria, and it loses some of the flocculating power overnight. The other starches must undergo preliminary transformations before the bacteriological action becomes apparent, so that deterioration is less rapid. Causticized solutions remain unchanged because the alkali inhibits the action of bacteria.

Table 12.—*Effect of Age of Solutions on Flocculating Properties*[a]

| Settling Reagent | Temperature of Reagent, Deg. C. | Lb. per Ton Solids[b] | | Settling Index, Sec. per Cm. | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Age Solutions, Days | | | | | | |
| | | Reagent | Caustic | 0 | 1 | 2 | 3 | 4 | 5 | 6 |
| Starch A | 80 | 1.1 | | 6.8 | 8.4 | 10.5 | 47.3 | 70.7 | | |
| Starch A | 100 | 1.1 | | 6.3 | 7.0 | 10.7 | 50.8 | 56.1 | | |
| Causticized starch A | 25 | 0.6 | 0.6 | 6.2 | 6.4 | 6.6 | 7.2 | 8.3 | 7.6 | 8.3 |
| Refined potato starch | 80 | 1.1 | | 9.4 | 8.8 | 9.1 | 9.1 | 11.0 | 44.0 | |
| Refined potato starch | 100 | 1.1 | | 6.4 | 6.5 | 6.7 | 6.9 | 12.3 | 23.3 | |
| Refined potato starch | 140 | 1.1 | | 4.8 | 4.4 | 5.0 | 5.2 | 6.0 | 7.0 | |
| Causticized refined potato starch | 25 | 0.6 | 0.6 | 6.8 | 6.3 | 6.0 | 5.8 | 5.8 | 6.0 | |
| Causticized refined potato starch | 60 | 0.6 | 0.6 | 4.5 | 3.8 | 4.3 | 4.2 | 4.3 | 4.4 | |
| Crude cornstarch | 80 | 1.1 | | 9.9 | 9.5 | 9.8 | 10.7 | 29.8 | 60.2 | |
| Crude cornstarch | 100 | 1.1 | | 6.6 | 7.3 | 7.2 | 6.8 | 27.5 | 39.8 | |
| Crude cornstarch | 140 | 1.1 | | 4.6 | 4.6 | 4.7 | 4.9 | 5.5 | 7.9 | |
| Causticized crude cornstarch | 25 | 0.6 | 0.6 | 9.7 | 7.3 | 7.1 | 7.6 | 7.0 | 7.3 | |
| Causticized crude cornstarch | 25 | 0.6 | 1.1 | 6.2 | 6.0 | 5.5 | 5.3 | 6.4 | 6.9 | |

[a] 5 per cent solids. Slurry temperature 29° C.

[b] To convert to parts per million multiply by 25.

## SUSPENSIONS SUCCESSFULLY FLOCCULATED WITH STARCH SOLUTIONS

During the investigation the treatment of a number of suspensions other than coal slurry was attempted. Among these were water suspensions of metalliferous ores, sewage, talc, clay, and a slime from a silver electroplating bath. The excellent results attained by various modifications of starch treatment on these suspensions indicate a wide applicability of such treatment. The experience gained in treating these different suspensions has shown clearly that at present there is no general method of starch treatment suitable for all types of suspensions. Lack of space prohibits a complete discussion of these results, but it can be said that proper consideration of the following conditions has made possible the successful treatment of all the suspensions encountered, either by the use of modifications of the starch treatment or by the use of electrolytes in conditioning the slurry for starch treatment:

1. Characteristics of solids
    - *a.* Gravity
    - *b.* Particle size distribution
    - *c.* Surface properties
2. Characteristics of water
    - *a.* Dissolved electrolytes
    - *b.* pH

Table 13 summarizes the more interesting results.

TABLE 13.—*Summary of Results Obtained from Starch Treatment of Various Suspensions*

| Type of Suspension | Settling Index, Sec. per Cm. | |
|---|---|---|
| | Untreated | With Starch Treatment |
| Iron ore | 18 (incomplete) | 2 (complete) |
| Talc ore | 14 (incomplete) | 3 (complete) |
| Gold ore | 32 (incomplete) | 2 (complete) |
| Electroplating slime | No appreciable settlement in 6 weeks | 5 (complete) |
| Sewage | 300 (incomplete) | 9 (complete) |

## CHEMISTRY OF STARCH IN RELATION TO FLOCCULATION

Starch occurs in two associated forms: amylopectin and amylose. Amylopectin occurs as the outer skin of the starch grain, while amylose is present as the contents of this envelope. The two differ principally in solubility. Amylose forms a colloidal solution when mixed with water and contains no phosphorus, while amylopectin is normally insoluble in water and contains chemically combined phosphorus. This phosphorus is present as a phosphoric acid ester of starch.

When starch grains are heated in water, the grains expand and rupture at a temperature that varies with starches from different sources. At this temperature, the amylose is released from the confining wall of amylopectin and passes into colloidal solution. Depending on the concentration of starch, the amylose may be dispersed as a gel or as a solution. Several investigators have shown that the gel-forming properties of starch are due to the amylopectin. It has further been shown by these investigators that the removal of the phosphate radical by hydrolysis and dialysis destroys this gel-forming property.

This provides one explanation for the results obtained in heating and causticizing starches. Table 14 compares the temperature of starch rupture as found with the point at which starch solutions acquire appreciable flocculating properties. The agreement between these figures shows that the first flocculating property acquired by the starch is probably due to the presence of colloidally dispersed amylose.

TABLE 14.—*Comparison of Temperature of Starch Rupture with Temperature at Which Flocculating Properties Appear*

| | Rupturing Temperature of Starch, Deg. C.[a] | Temperature at Which Flocculating Properties Appear, Deg. C. |
|---|---|---|
| Cornstarch | 55.0 | 56 |
| Potato starch | 50.7 | 52 |

[a] After Pringsheim.

It has been previously shown that a starch solution has attained only a part of its flocculating properties at the rupturing temperature. It is assumed that the additional flocculating power resulting from higher temperatures is due to changes in the amylopectin. Organic esters are, as a rule, rather easy to hydrolyze either by pressure heating or treatment with acid or alkali. Thus one explanation for this increase in flocculating power would be the hydrolysis of the phosphoric ester of starch (amylopectin) to form soluble amylose and phosphoric acid.

Other investigators have further shown that heating starch at temperatures in excess of 145° C. results in further hydrolysis of the starch into the various decomposition products (dextrins). This provides a ready explanation for the decrease in flocculating power of starch solutions when heated above 145° C.

## SUMMARY

Starch solutions capable of flocculating finely divided solids suspended in water can be prepared either by heating under pressure in the range of 100° to 160° C. or by causticizing starch paste. Maximum efficiency with a noncaustic solution is attained when the reagent is prepared at 140° to 145° C. Causticizing temperature depends on the strength of caustic solution used. At 25° C. an efficient reagent can be produced with a 2.5 per cent solution of commercial NaOH. Starch reagent can be prepared most economically by causticizing or heating a 5 per cent starch paste with thorough mixing and diluting. Any starch can be used to prepare a flocculating reagent, but potato starch is recommended. Solutions prepared by heat alone will retain their properties for three days. Causticized solutions retain their properties for two weeks or longer. The use of these flocculating reagents appears to have a wide range of application.

## ACKNOWLEDGMENT

The authors wish to acknowledge the assistance of Messrs. P. S. Gardner, Sr., P. S. Gardner, Jr., C. Q. Campbell, S. B. Barley, William Robert and George Black, and also the aid of the literature on the subject cited in the bibliography.

They are indebted to Mr. J. B. Morrow, Production Vice-President of the Pittsburgh Coal Co., for his suggestions, and to Mr. D. H. Davis, Chief Chemist of the Pittsburgh Coal Co., for his aid in preparation of the manuscript.

## BIBLIOGRAPHY

1. W. R. Chapman: Treatment of Fine Coal and Slurry at Coke Ovens and Collieries. *Iron and Coal Trades Rev.* (1933) **126,** 834.
2. D. T. Davies and E. T. Wilkins: Continuous Clarification of a Coal Washery Circuit with Glue. *Fuel in Science and Practice* (1935) **14,** No. 2. Excerpts in *Coll. Guard.* (1935) **152,** 521.
3. C. W. Dawsett: Gold Precipitation Improved by Adding Caustic Starch. *Min. and Met.* (1936) **17,** 105.
4. H. T. Durant and W. Cullen: Separation of Solids from Liquids: Thickening. *Coll. Guard.* (1934) **151,** 1192–1195.
5. G. E. Foxwell: Treatment of Washery Water. *Coll. Engr.* (1935) **12,** 364–366.
6. R. D. Gifford: Clarification of Polluted Water with Particular Reference to Colliery Waste and Sewage. *Inst. Engrs., Jnl. and Rec. Trans.* (1934) **44,** pt. 10, 477–493. See also *Coll. Guard.* (1934) **148,** 350–351.
7. G. Graef: Newartiges Waschwasser-Klaerverfahren im Steinkohlenbergbau. *Glückauf* (1932) **68,** 304–306. Translation in *Iron and Coal Trades Rev.* (1932) **124,** 765.
8. C. W. H. Holmes: The Clarification of Washery Water. *Coll. Engr.* (1935) **12,** 40–42, 58, 79–82, 133–135.
9. C. W. H. Holmes: The Riddle of the Slimes. *Coll. Engr.* (1937) **14,** 399–402.
10. F. K. T. Van Iterson: Clarification of Coal Washery Effluent. *Proc.* Royal Netherlands Acad. Amsterdam (1938) (Reprint) **41,** No. 2. 13 pp. and bibliography.
11. J. L. Lewis: Clarification of Washery Water and Recovery of Coal Slurry. *Coll. Guard.* (1935) **151,** 895–898.
12. L. W. Needham: Settling of Fine Coal in Water. *Coll. Guard.* (1930) **141,** 124–128.
13. L. W. Needham: Collection and Treatment of Washery Slurry. *Coll. Guard.* (1931) **143,** 2044–2046, 2133–2134. See also *Iron and Coal Trades Rev.* (1931) **123,** 907.
14. L. W. Needham: Treatment of Washery Water—Practical Aspects of Flocculation. *Coll. Guard.* (1936) **153,** 191–197. Discussions by D. H. C. Briggs, N. E. Webster and W. E. Raybould, *idem,* 248, 530–531.

15. M. E. Nicklin: Solving the Slurry Problem. *Coll. Guard.* (1933) **147,** 1210–1212; *Gas World* (1934) **100,** 18–20.
16. W. Petersen: Adsorption of Xanthagonates in Coal Sludge. *Kolloid Ztsch.* (1930) **42,** 174–177. In German.
17. W. Petersen: Die Klaerung von Braunkohlen-Schlaemmen. *Braunkohle* (1932) 851–854.
18. W. Petersen and F. Gregor: Die Klaerung des Schlammwassers aus Kohlen waeschen. *Glückauf* (1932) **68,** 621–630. Translation in *Iron and Coal Trades Rev.* (1932) **125,** 160.
19. W. Petersen: Plant Test on Clarification of Slurries from Stone Coal Preparation Plants. *Glückauf* (1934) **70,** 125–131. In German.
20. W. E. Raybould: Conditioning of Washery Water: Flocculation. *Trans.* Inst. Min. Engrs. (1934) **88,** 194–229.
21. J. E. Samuel: Flocculation of Washery Water. *Coll. Guard.* (1932) **145,** 939–941, 985–987.
22. J. O. Samuel: Some Aspects of Flocculation. *Chem. and Ind.* (1936) **14,** 669–680.
23. J. O. Samuel: Theoretical and Commercial Aspects of Flocculation. *Chem. Age* (Lond) (1938) **38,** 201–203.
24. J. Sinclair: The Hoyois Washery at Rockingham Colliery. *Coll. Guard.* (1935) **150,** 887–889.
25. E. Tomalin: Flocculation of Coal Slurries. *Jnl.* Soc. Chem. Ind. (1937) **56,** pt. 1, 384T–389T; (1938) **57,** pt. 2, 175–179.
26. R. J. Venn: Recovery of Fine Coal from Washery Effluents. *Mech. World* (1936) **99,** 183–184.
27. E. T. Wilkins: Sensitization and Other Observations on Slurry Flocculation. *Jnl.* Soc. Chem. Ind. (1935) **54,** pt. 1, 391T–393T.
28. Slurries: Inst. Min. Engrs., Utilization of Coal Committee, *Memo.* No. 14 (1934) 4 pp. See also *Coll. Guard.* (1934) **148,** 822–823; *Iron and Coal Trades Rev.* (1934) **128,** 728; *Fuel Economist* (1934) **9,** 362–364; and *Engineering* (1934) **137,** 745.
29. Clarification of Washery Water. Excerpts of *Memo.* No. 15, Utilization of Coal Committee of the Inst. Min. Engrs. *Coll. Guard.* (1934) **149,** 196.
30. Flocculation of Slurries. Excerpts from Annual Report of Fuel Research Board for 1933–34. *Coll. Guard.* (1934) **149,** 1004.
31. New Type of Water Clarifier for Coal Washeries. Abstract translated from *Mines, Carriers, Grandes Entreprises. Coll. Guard.* (1930) **140,** 1554–1555.
32. Treatment of Coal Slurry. Experiments at Emlyn Anthracite Colliery (Unifloc Treatment). *Iron and Coal Trades Rev.* (1935) **131,** 233–235.
33. Coal Cleaning and Grading Plant at the Rising Sun Pit. *Iron and Coal Trades Rev.* (1935) **131,** 896–899.
34. Flocculation in Theory and Practice. *Coll. Engr.* (1936) **13,** 45–52.
35. H. Pringsheim: Chemistry of the Monosaccharides and of the Polysaccharides. New York, 1932. McGraw-Hill Book Co.

## DISCUSSION

*(G. B. Gould presiding)*

R. D. SNOUFFER,* Library, Pa. (written discussion).—Most of my work has been done with a standardized reagent and the amount and the method of treatment varied. The "standard reagent" used was a 1 per cent causticized starch, prepared by rupturing a cold 4 per cent potato-starch suspension with an equal amount of 4 per cent sodium hydroxide. The resultant gel was stirred, mechanically, for at least 10 min. and was then diluted with an equal volume of water to give the 1 per cent caustic starch reagent.

---

* Lubrication Engineer, Pittsburgh Coal Co.

In conducting the tests, an instrument was needed to measure relative turbidity, which is a measure of the difference in degrees of flocculation. This was done with the aid of an optical photometer and from these data curves were drawn that showed optimum concentrations and trends with varied treatments.

The vast majority of my work and that of the authors checks very well in the essentials, but I wish to add these words on a few points:

1. The compactness of the thickened slurry is an inverse function of the amount of reagent added. If very little starch is used, or none at all, the rate of clarification is very slow but the settled material is compact and is not readily shaken into suspension. As the amount of starch is increased, the size of the flocs and the percentage of water in the settled product increases, thus allowing the flocs to be readily channeled by fast-moving water or again brought into suspension.

2. With treatment up to the amount that gave the optimum result, there was no sign of starch in the clarified water when tested with an iodine solution. As this is a very sensitive test, it shows that the starch was being completely removed by the coal particles. When amounts of starch were used that were in excess of the optimum range, a blue color due to residual starch was obtained in the water when the iodine was added.

3. No verification of the effect of pH can be made from my investigation, for the caustic-starch reagent apparently worked almost equally well in all waters having pH values ranging from below 6.0 to as high as 13.0.

4. Some plants employ ferric or magnesium hydroxides as flocculants and the method followed is to add reagents such as magnesium or ferric chloride with lime to the water undergoing treatment. As many washery waters contain magnesium or ferric chloride in solution, the only reagent added is the lime. The major inherent difference between methods using the hydroxides and those using starch is that the gelatinous flocculant is formed from true solution in the first case while in the latter it is added to the system. This accounts for the need of pH control with most reagents and the negligible control needed with the starch. However, all the pH values tried lay above the iso-electric point of the starch, which is about 4.6.

5. Often clay can be held in suspension by adding sodium hydroxide, but by introducing a small amount of starch into a basic slip, rapid and complete coagulation of the clay took place. Mixtures of clay and coal seem to flocculate equally well, indicating that separation of the two by preferential flocculation may be difficult.

6. Until near the end of my investigation there was close agreement with the general belief that the starch reagent must be freshly prepared and that it deteriorates with age. Further study showed that the opposite was true, and this substantiates the statement of Gardner and Ray that causticized starch solutions remain unchanged with age.

It was found that when using a freshly prepared 1 per cent causticized starch reagent minimum turbidity was reached on adding 10 to 15 parts per million, as is shown by Fig. 1. Amounts either greater or less gave an increased turbidity, the rise being greatest with a decrease in treatment. A normal curve, Fig. 2, resulting from the use of reagents differing only in age, showed a progressive increase in turbidity, when using equal amounts of treatment. Tests run on reagents from one to fourteen days old showed that the optimum amounts of treatments were less than for a fresh reagent. This shown in Fig. 3, and indicates that the increase in turbidity when using old solutions was due to an increase in activity of those solutions, and that the progressive rise in turbidity was due to overtreatment rather than to deterioration of the reagent. It is to be noted here that the minimum turbidities obtainable with the older reagents were slightly higher than those obtained from the freshly prepared solution, but this, however, does not seriously impair their use.

7. When the starch reagent is added to the coal suspension the particles form aggregates or flocs, in which the coal particles are partly surrounded by the starch sol. The charge on the coal particle being negative and that of the emulsoid being positive, there are local shieldings of electronic forces. If a very limited amount of starch is added, the coal is "sensitized," while if more starch reagent is used "coagulation" of the coal takes place. Still higher concentrations of reagent can result in stabilization, if added so as to produce this effect, as was shown by the increase in turbidity by overtreatment.

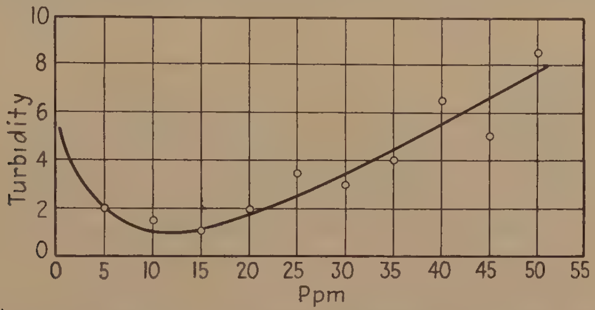


FIG. 11.—CONCENTRATION OF FRESHLY PREPARED CAUSTICIZED STARCH.

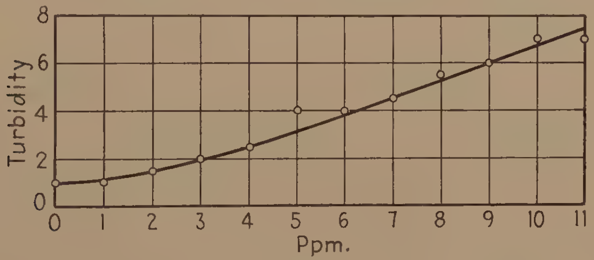


FIG. 12.—EFFECT OF AGE OF REAGENT AT EQUAL CONCENTRATIONS (10 PARTS PER MILLION).

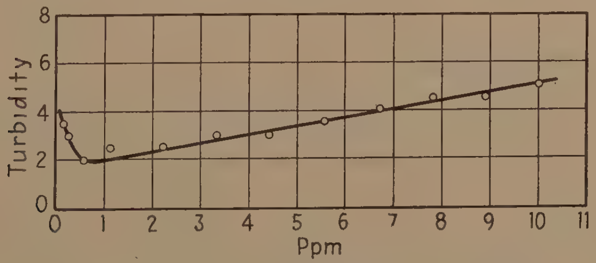


FIG. 13.—CONCENTRATION OF CAUSTICIZED STARCH SEVEN DAYS OLD.

8. The practice of putting into the flocculating basin all at one time an amount of reagent that has been calculated as satisfactory for treatment in a day's run is not advisable. Such an addition would result in a period of stabilization of the finest material, and as the excess starch was removed from the system an efficient clearing condition would be reached, followed in turn by a period through which the solid content of the system would start to rise.

9. To promote the most satisfactory flocculation, the causticized starch should be continuously added and rapidly agitated for a few seconds, to make sure of complete and uniform distribution throughout the entire suspension. This short period should then be followed by a longer period of gentle mixing so that conditions may favor the gathering together of these particles into large flocs.

D. F. Irvin,* New York, N. Y. (written discussion).—Slime flocculation by use of causticized starch gave such impressive results in the coal-preparation plants of the Pittsburgh Coal Co. that efforts were made to extend its benefits to finely ground pulp of gold-cyanidation plants.

In some such cases, slime conditions exist, which produce slow settling and filtering rates. There is the added condition, absent from coal preparation, wherein valuable gold-cyanide solution must be recovered from the finely divided ore particles.

Tests were made on settling and filtering behavior at a gold-ore cyanide plant where the pulp was notably hard to settle and filter. The best results are believed to typify use of causticized starch as a coagulant on slime from gold-cyanide plants. In general, when using causticized starch, the slime pulp settled much more rapidly than when starch was not used. However, the ultimate pulp density of the slime was somewhat greater when starch was not used, although considerably more time was needed to attain this point. Clarity of the supernatant solution was better when causticized starch was used as a coagulant. A marked difference was observed in the appearance of the thick, settled pulp resulting from use of starch. It was perceptibly "stiffer," and thus showed coagulated effect very plainly. This coagulated pulp gave unusually good filtering performance, as compared to pulp that had received only the ordinary coagulation by lime. The starch-treated pulp gave some increase in dry weight handled per unit filter area; considerable reduction in moisture content of filter cake, and particularly the removal of cake from surface of filter, was much more satisfactory. These tests did not include washing of the cake to remove gold-cyanide solution. A thorough application of this method to cyanidation pulps on a full-scale basis has not yet been arranged, which is regrettable, since it showed promising possibilities for difficult pulps.

Materials that settle and filter easily seldom need starch coagulation.

There has been a general reluctance to make use of any such method on which patent coverage is claimed, as that would require licensing from patentee. This has been a definite hindrance, but such feeling will probably persist, except for some isolated cases where settling and filtering might be very troublesome, and the use of starch as a successful coagulant might justify special arrangements to use the method.

---

* Oliver United Filters, Inc.

# Mineralogical Characteristics Affecting the Concentration of a Semioxidized Lead-silver Ore

By R. E. Head,* Member A.I.M.E.

(New York Meeting, February, 1938)

Some mixtures of sulphide and oxide ores from the Tintic district in Utah are of a sufficiently good grade to be shipped to the smelter without beneficiation. In mining this type of ore, however, a material tonnage of ore of a similar composition but of lower grade is obtained. It is a question of economics whether such ore should be shipped with a certainty of a small return or concentrated if that would yield a sufficiently increased return to amortize plant construction and upkeep and yield a higher rate of profit than at present. It may be assumed that the tonnage of this borderline ore is constantly increasing and that eventually it will attain such proportions as to justify plans for milling on a relatively large scale. Under existing conditions, the producer of mixed sulphide and oxide ores is not greatly concerned about the physical characteristics of his ore or of its mineralogical complexities, since his contract with the smelter calls for payment on the basis of chemical analysis.

When concentration is contemplated an entirely different picture is presented. Percentages of valuable metal content must then be considered in terms of minerals, for it is in the form of minerals that recoveries are made and losses sustained. In describing the performance of a given flotation mill and reagent combination, it may be stated as a generality that a specific percentage recovery of valuable elements is made. Technically, however, the concentrator is really constructed and the reagents are selected to recover the valuable minerals.

These considerations must be given prominence in discussing borderline ores from the Tintic district because of their physical characteristics and mineralogical composition. Because of these peculiarities they may be justly termed complex, since their lead, silver, and copper contents are each represented by two or more minerals of different chemical composition and presenting widely divergent physical properties. This paper sets forth the results of a microscopic study of a type of borderline ore from the Tintic district that is now being treated by direct smelting. A

---

Published by permission of the Director, U. S. Bureau of Mines. Manuscript received at the office of the Institute Dec. 29, 1937. Issued as T.P. 939 in Mining Technology, July, 1938.

* Microscopist, Metallurgical Division, U. S. Bureau of Mines, Salt Lake City, Utah.

description of the minerals in the ore is given with particular reference to their modes of occurrence, distribution, and physical characteristics. The description of the lead and silver minerals sets forth hitherto unpublished facts, which are of great importance since any process for treating this ore must effect a high recovery of these minerals to justify its adoption and insure economic operation. The analysis of a typical sample (Table 1) represents the chemical composition of ore whose physical and mineralogical characteristics are discussed in detail. The analysis of a tailing resulting from its flotation is given also in Table 1. Comparison of the head and tailing analyses emphasizes the need for a higher recovery of the silver and lead in the ore, since these minerals represent relatively high losses, and such a product would contribute materially to economic waste.

TABLE 1.—*Analysis Sulphide-oxide Ore and Flotation Tailing*

| | Ounces | | Per Cent | | | | |
|---|---|---|---|---|---|---|---|
| | Au | Ag | Pb | Cu | Fe | S | Insol. |
| Ore | 0.045 | 22.00 | 4.6 | 0.34 | 11.2 | 6.4 | 68.1 |
| Flotation tailing | 0.017 | 5.70 | 3.8 | 0.10 | 7.6 | 0.8 | 77.0 |

## GENERAL MINERALOGY OF THE ORE

The mixed ores from the Tintic district contain a relatively large variety of minerals because considerable oxidation has taken place and many secondary products have been formed. Lead is present as galena, anglesite, cerussite and plumbojarosite. Silver occurs in the metallic form, in tetrahedrite, pearcite and argentojarosite. The copper is represented by chalcopyrite, chalcocite, enargite and tetrahedrite. This list can be considerably enlarged by mention of numerous rarer minerals such as bendheimite, limonite, brochantite, mimetite, and others. These minerals, however, do not represent any material amount of metal and are of interest chiefly because of their geological or mineralogical significance. Their recovery or loss would not greatly influence the grade of products made or the general metallurgical results attained. The ores contain a considerable amount of pyrite and oxidized iron minerals, together with quartz, limestone, and the products of rock decomposition. Oxidized iron and rock-decomposition products may be considered as primary slime-forming constituents and potential sources of difficulty during the treatment of the ore.

## RESULTS OF CONCENTRATION TESTING

Numerous flotation tests have been made on the Tintic mixed ores by various interested persons, and it has been definitely established that good recoveries of the sulphide minerals can be made. The tailing losses therefrom are largely represented by oxidized minerals, together with a relatively small quantity of sulphide minerals that have escaped recovery. The mineralogical and physical characteristics of the oxide minerals are of major interest since their recovery constitutes the problem involved in successfully concentrating the ore.

## Oxidized Lead Minerals

Microscopic study of numerous hand samples of the ore and of products made during experimental testing indicates that anglesite and cerussite contain the bulk of the lead lost in the tailings. Although much advance has been made in the art and practice of flotation, the recovery of oxidized lead minerals from the mixed ores still remains an unsolved problem. The anglesite and cerussite in the Tintic ores are normal types of the two species and no indications of peculiarities either in chemical composition or physical characteristics were observed during the study.

It is not possible to state which of the two minerals occurs in greater abundance, since the study of hand specimens and concentration products indicate considerable variability of occurrence. Mention of this factor is made because of the inherent differences in the two minerals during grinding and in the flotation cell. Cerussite is brittle, and shatters into small particles during crushing, forming a granular slime. Anglesite of the noncrystalline variety has no definite cleavage and breaks down easily into extremely small particles that are notably "sticky" and wet and, if present in sufficient quantity, have a marked tendency to attach themselves to other constituents in the ore in the form of slime coatings. Examination of tailings, using a staining method[1] to differentiate between cerussite and anglesite, indicates that anglesite is the more difficult mineral to float, and since it is known that anglesite does not respond satisfactorily to sulphidizing, this fact probably accounts largely for its greater abundance in the tailings examined.

Anglesite and cerussite are distributed through the ores in a fairly uniform manner, but their liberation by crushing is not difficult and may be readily accomplished by grinding to 150 mesh. However, in grinding the low-grade ore, which is hard and siliceous, anglesite and cerussite are reduced to the slime sizes, making them difficult to recover by flotation. In the slimed condition these two minerals are not amenable to treatment by gravity methods, hence their recovery presents one of the chief problems for solution in concentrating the borderline ores.

Jarosite minerals are relatively abundant in the ores because of the conditions under which oxidation has taken place. Their distribution is fairly uniform and they are difficult to distinguish with any degree of certainty because of their association with oxidized, ocherous iron and their general similarity in appearance. The lead, silver and iron forms of jarosite are of common occurrence, and since they exist as yellow hexagonal crystals of very small size, regardless of their differences in chemical composition, they have not yet been differentiated by optical methods. Chemical dissolution tests made on the semioxidized ores indicate that jarosites account for an appreciable amount of lead and a very material quantity of silver. Although the floatability[2] of the jarosites has been studied, it cannot be said that much is definitely known concerning their characteristics, since the work done was of a preliminary nature and was not continued to completion.

---

[1] References are at the end of the paper.

## Occurrence of Silver

Silver is the most valuable constituent in the borderline ores and any successful process for treating the ore must insure a high recovery of silver. In the sulphide portion of the ore, tetrahedrite is the chief silver-bearing mineral. Minor amounts of pearcite ($9Ag_2S \cdot As_2O_3$) have been identified in the ore, together with other rare species of silver-bearing minerals, but the amount of silver thus represented is so small as to be virtually negligible. Although the galena in the Tintic ore is silver-bearing to a slight extent, its percentage relationship to the total silver in the ore is on the same order as that in the rare minerals. Metallic silver constitutes more than 80 per cent of the silver content of the borderline ore under discussion, and its mode of occurrence renders it extremely difficult to recover. Although it has been stated by other investigators that metallic silver occurs in the Tintic ore and that both anglesite and cerussite are known to be silver-bearing, the actual associations of the metallic silver have never been conclusively determined so far as is known by the writer.

The present study has developed definitely and conclusively that cerussite and anglesite in the Tintic ores are carriers of metallic silver. Fire assays of a high-grade, massive specimen of anglesite showed a silver content of 49.1 oz. per ton, and samples of cerussite assayed from 36.2 to 43.3 oz. per ton. Examination of these specimens under the binocular microscope, at a magnification of 100 diameters, failed to show any indication of silver. Specimens of cerussite and anglesite were impregnated with Bakelite to render them hard enough to be polished for critical study in reflected light on the metallographic microscope at higher magnifications. Under these conditions innumerable small specks of metallic silver were found in both cerussite and anglesite. The size of the particles varied from an average maximum of 74 microns (200 mesh) to from one to three microns. Some specks were of a size barely visible at a magnification of 500 diameters and appeared as mere glints of light. A study of polished specimens showed that silver was definitely concentrated in various portions of both anglesite and cerussite (Fig. 1). In these areas, the specks of metallic silver were abundant as compared to other areas that were barren or where only occasional specks of silver were sparsely distributed. Checking over the distribution of the metallic silver in these specimens under the binocular microscope made plain that the notable concentrations of silver were confined to dark colored portions of the specimens. Barren portions and areas in which little or no silver was visible were invariably light in color. This statement applies to both anglesite and cerussite.

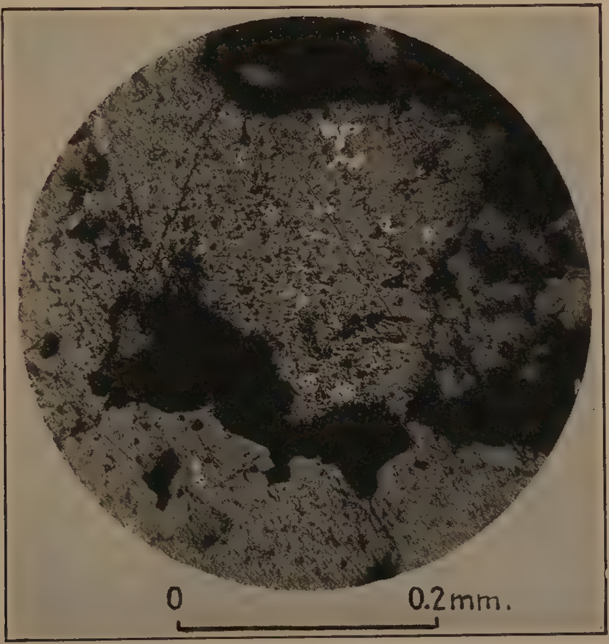


Fig. 1.—Metallic silver in lead carbonate. × 150.

Large black areas are holes. White specks show metallic silver. Gray indicates lead carbonate.

The largest silver particles in the field are 0.03 mm. or 30 microns (smaller than 400 mesh). The smallest particles visible are approximately one micron or the equivalent to the openings in a theoretical 9200-mesh sieve. Both anglesite and cerussite contain silver particles too small to be liberated by grinding, hence losses of these two minerals in tailing entail a possible loss of silver.

Additional proof of the segregation of silver in the dark colored areas of the two minerals was obtained by fire assay. Coarse granular samples of anglesite and cerussite were separated into light and dark fractions under a high-power hand lens. But a crude separation resulted from this procedure, since complete liberation of the two types of mineral had not been affected, and the particles selected for assay contained many middling grains that were mixtures of both dark and light minerals. However, the fire assays substantiated the microscopic evidence of segregations in a conclusive manner, as shown in Table 2.

The results show a decided difference in the silver content of the light and dark varieties in coarsely crushed ore. Since the microscopic study of polished surfaces has shown that areas barren of silver exist in both the sulphate and carbonate lead, one might predict that assays made on segregated 200-mesh particles of the light and dark varieties would show a still wider variation in silver than the examples cited. As a matter of interest on this subject, assays made on a very light colored sample of virtually pure cerussite from the Alta district, which was devoid of dark colored inclusions, showed but a trace of silver. While discussing the silver-bearing characteristics of light and dark colored cerussite and anglesite, it should be emphasized that the dark colored areas in the minerals studied were not residual sulphide inclusions.

TABLE 2.—*Fire Assay of Selected Anglesite and Cerussite*

| Mineral | Light Silver, Oz. | Dark Silver, Oz. |
|---|---|---|
| Cerussite | 32.7 | 81.5 |
| Anglesite | 19.7 | 48.35 |

## INFLUENCE OF MINERALOGY ON CONCENTRATION

The mineralogical composition of the semioxidized ores from the Tintic district and the association of the various minerals are the most important factors for consideration in working out a process for their concentration. High recoveries of lead and silver are imperative, regardless of whether some of the ores now being shipped to the smelter are treated along with borderline ores or beneficiation is confined exclusively to low-grade material. The mineralogy is sufficiently similar in the two types of ore so that the attainment of satisfactory results in concentrating the low-grade ores would yield increased returns when applied to the borderline ores. Obviously, the types of ore treated and the tonnage involved are factors governed by definitely established economic considerations.

Records of experimental flotation tests made on typical samples indicate that satisfactory recoveries of the sulphides in the ore can be made by flotation. It should be emphasized, however, that the pyrite in these ores must not be disregarded. Although this mineral is not silver-bearing, the microscopic study of hand specimens and of crushed ore shows that tetrahedrite, which is a carrier of silver, is intimately associated with it. An appreciable quantity of tetrahedrite therefore may be locked with the pyrite when the ore is crushed to minus 150 mesh, at which size the anglesite and cerussite are liberated. The recovery of pyrite must be attained together with that of galena, free tetrahedrite, and the other sulphide minerals.

In considering the facts presented regarding the size of the metallic silver particles associated with the anglesite and cerussite, it is evident that the greater portion of these silver particles will remain locked with these minerals when normal grinding for flotation is practiced. Losses of anglesite and cerussite must necessarily be considered as possible losses in silver in addition to lead, depending on whether they happen to be barren of silver or contain included metallic particles. Examination of briquetted anglesite and cerussite grains panned from tailings has definitely shown that barren grains and silver-bearing grains are common. Because of this condition, the practice so common among metallurgists of assuming that the recovery of a given amount of lead should involve a corresponding ratio of silver recovery will lead to faulty conclusions. The fact has been definitely established that the distribution of silver in anglesite and cerussite is by no means uniform. If the silver were chemically combined instead of being mechanically associated, the ratios of oxide lead lost might be calculated in terms of silver with some approximation of accuracy. Furthermore, there is some basis for entertaining the possibility that the dark colored grains of lead carbonate and lead sulphate that are known to contain concentrations of metallic silver may have differing rates of floatability. An unfortunate balancing of reagents might cause "reverse selectivity," and lead to an increased recovery of barren particles over those containing silver, or vice versa.

In grinding the ore to 150 mesh, it is certain that some portion of the metallic silver is liberated, especially from the anglesite, because of the inherent tendency of the lead sulphate to slime. Free metallic silver particles have been found in both concentrates and tailings during the microscopic studies. This indicates that the floatability of the liberated silver cannot be predicted with any degree of certainty. Microscopic examination of metallic silver particles in concentrates showed that their surfaces were relatively clean. The surfaces of silver particles in tailings were invariably dirty or virtually obscured. These facts suggest that silver released from cerussite is cleaner and therefore more readily recoverable than that freed from the anglesite. Cerussite is a brittle mineral having a definite cleavage and the bond between such crystalline surfaces and those of metallic silver should break sufficiently clean to produce the maximum number of uncontaminated silver particles. In considering the opposite physical characteristics of anglesite, the production of silver particles having surfaces free from associated lead sulphate seems improbable.

## JAROSITES

The distinguishing characteristics of jarosite minerals render their visual identification a fairly easy matter. However, optical methods have not yet been developed for differentiating between the jarosites of lead, silver and iron. The jarosite formula $RO \cdot 3Fe_2O_3 \cdot 4SO_3 \cdot 6H_2O$ is of interest since *R* may represent iron, potassium, sodium, ammonium, lead or silver. The analyses by Schaller[3] and Schempp[4] in Table 3 may be accepted as a standard for considering the lead and silver content of plumbojarosite and argentojarosite. It is known that the semioxidized Tintic ores contain lead, silver and iron-bearing jarosites, but as yet no dependable method, chemical or otherwise, has been developed for determining the relative amounts in which these minerals occur. Attempts to determine the amount of silver occurring as argentojarosite have indicated that a material amount of it exists in this form, although the method employed is considered as an approximation only.

TABLE 3.—*Analyses of Jarosites*[3,4]

| PLUMBOJAROSITE (BEAVER COUNTY, UTAH), PER CENT | |
|---|---|
| $PbO$ | 18.32 |
| $Fe_2O_3$ | 42.11 |
| $K_2O$ | 0.13 |
| $Na_2O$ | |
| $SO_3$ | 27.59 |
| Insoluble | 2.64 |
| $ZnO$ | 0.30 |

| ARGENTOJAROSITE, PER CENT | |
|---|---|
| $Ag_2O$ | 18 |
| $Fe_2O_3$ | 43 |
| $SO_3$ | 28 |
| $H_2O$ | 10 |

The floatability of plumbojarosite and argentojarosite introduces a factor of uncertainty in treating the Tintic ores. Although some research has been conducted with the object of determining the reagents most suitable for floating them and the conditions most favorable for effecting their recovery, little definite information on this subject exists. The lead content of plumbojarosite is relatively low and the extent to which its recovery or loss would affect operations is a matter of conjecture. There is evidence to support the belief that both plumbojarosite and argentojarosite float more readily as unit crystals than in clumps or aggregates. The jarosite minerals occur as minute crystals, and when distributed through a pulp containing slimes made up of iron and other oxidized material it is obvious that reagent combinations suitable for recovering them must possess a high degree of selectivity.

In considering the difficulties involved in concentrating the free metallic silver, together with that still combined with anglesite and cerussite, one is impressed with the complexity of the Tintic semioxidized ore. The mineralogical facts determined during the study of this particular type of ore indicate the causes for the difficulties that have beset experimental work. They constitute the important basic factors in a problem, whose solution must be attained before success is possible by flotation methods. The flotation of mixed sulphide-oxide ore yet remains an unsolved problem, especially when the metallic values are represented by complex occurrences of minerals having widely different physical and chemical characteristics.

## SUMMARY

Stripped of detailed descriptive matter, the factors controlling the concentration of this type of semioxidized ore from the Tintic, Utah, district are summarized in the following statements:

1. The ore studied is made up of a complex mixture of sulphide and oxide minerals possessing widely different physical and chemical characteristics. A high recovery of each of these minerals must be made to attain economically acceptable results.

2. Silver, which represents the chief value in the ore, occurs largely in the metallic form as minute particles in anglesite and cerussite. A material portion of silver is combined as argentojarosite, a mineral known to be difficultly floatable, especially when intermixed in a pulp containing oxide iron and products of rock decomposition. Some lead also occurs as plumbojarosite, which possesses characteristics similar to argentojarosite.

3. Although crushing to 150 mesh liberates the major portion of the valuable minerals, grinding the entire ore to this size complicates concentration by producing lead sulphate and lead carbonate slimes that are difficult to float.

4. Anglesite and cerussite particles lost in tailings may represent a silver loss because of the metallic silver associated with them.

5. Relatively high concentrations of metallic silver exist in the dark colored lead sulphate and lead carbonate. The dark and light varieties of these minerals do not float alike, thus introducing the possibility that a given reagent combination of flotation reagents might preferentially float the light colored anglesite and cerussite, which contain relatively low silver and reject the dark colored or richer varieties.

6. Although some metallic silver is liberated during grinding, a portion of it does not float readily because of partly obscured and contaminated surfaces. It is believed that this refractory silver was originally associated with anglesite.

7. All the sulphide minerals in the ore must be floated, including pyrite, which contains inclusions of silver-bearing tetrahedrite.

In considering the complex mineralogy of the Tintic semioxidized ore, the reasons for the difficulties encountered have been stated. The Tintic ore is by no means an isolated example, since other ores of a similar composition exist and present the same difficulties of treatment.

## REFERENCES

1. R. E. Head and A. L. Crawford: A Staining Method for Distinguishing Cerussite and Anglesite in Ores, Concentrates and Tailings. U. S. Bur. Mines *R.I.* 2932 (1929).
2. R. E. Head and F. E. Thackwell: Progress Reports, Metallurgical Division—Floatability of Lead and Silver Jarosites. U. S. Bur. Mines *R.I.* 3275 (1935).
3. W. T. Schaller: Mineralogical Notes, Series 2. U. S. Geol. Survey *Bull.* 509 (1912) 82.
4. C. A. Schempp: A New Silver Mineral. *Amer. Jnl. Sci.* (1923) [5] **6**, 73–75.

## DISCUSSION

(*C. H. Benedict presiding*)

C. E. Locke,* Cambridge, Mass.—I was surprised to learn that Mr. Head had identified this silver as metallic silver. Had that been suspected or known before?

C. W. Davis,† College Park, Md.—It had been suspected and, I think, reported, but no one was certain. It could not be panned, but Mr. Head was able to show definitely that metallic silver occurs as minute particles.

C. E. Locke.—Has not that been of material assistance in attacking this problem, knowing what you have to deal with?

C. W. Davis.—That is what I intended to bring out,‡ the fact that he knew the minerals contained this material served as a starting point. Mr. Zimmerley went on with this start and found that he could treat the various minerals, and finally that he could treat the ore by grinding with iron balls in brine.

Member.—What strength of brine solution was used?

C. W. Davis.—A series of experiments was made, of which a report was issued in the Bureau of Mines *R.I.* 3364.

Member.—What is the chemistry of that operation?

C. W. Davis.—The lead and silver dissolved in the brine are precipitated as sponge metal by the clean metallic iron surfaces of the balls used in grinding.

E. C. Peterson,§ Santa Barbara, Chihuahua, Mexico (written discussion).—An enigma that has been disconcerting to the metallurgist working with the oxidized and semioxidized ores of the Tintic district has been largely, if not completely, solved by the findings of Mr. Head as reported in this paper. The failure of lead and silver recoveries to follow each other proportionately into the concentrate (or conversely, the losses to follow proportionately into the tailing) is explained by the presence of metallic silver, which occurs as fine disseminations in the cerussite and the anglesite of the ore. Heretofore, such discrepancies, which were widely variant in a given ore or among several ores of the district, were assigned to the supposed presence of argentojarosites and plumbojarosites. Although the occurrence of a dark variety of anglesite was noted, particularly in the ore from the North Lily mine, a higher silver concentration in this variety or within dark areas of the mineral was not known. For his outstanding contributions to this problem, Mr. Head is to be congratulated. However, I should like to ask several questions:

1. Inasmuch as "the surfaces of silver particles in the tailing were invariably dirty and virtually obscured," it is suggested that these particles have been released from the anglesite and not from the cerussite. In addition to this probability, which is based on the physical characteristics of anglesite, is it not equally probable that the surface of the metallic silver is obscured in consequence of contamination during grinding? Several years ago, Oldright and Head found that prolonged grinding

---

* Professor of Mining and Ore Dressing, Massachusetts Institute of Technology.

† Assistant Chief Engineer, Metallurgical Division, U. S. Bureau of Mines.

‡ Mr. Davis presented the paper in the absence of the author.

§ Metallurgist, Cia. Minera Asarco, S. A.

rendered free gold particles less amenable to flotation.[5] Inasmuch as Mr. Head does not detail his procedure in grinding the ore to 150 mesh, I feel that this is an interesting point in question.

2. The surfaces of the silver particles in the concentrate were found to be relatively clean. Was flotation concentration effected by the use of sodium sulphide as the sulphidizer? (I realize that the particles were of minute size, yet this following question may have an answer.) If so, did the microscopic examination of the surfaces of the metallic silver particles in either the concentrate or the tailing show a silver sulphide film or give evidence that such a film had been formed and then had been partly or wholly removed by attrition during flotation or other agitation of the pulp?

R. E. Head (written discussion).—It is scarcely possible to account accurately for the contamination of silver particles that have been released during the grinding of the type of ore in question. There are, however, at least three possibilities worthy of consideration. As a primary basis it is well to consider the appreciable increase in volume involved in the alteration of galena to anglesite and to cerussite. When galena alters to the sulphate there is an increase in volume of approximately 53 per cent and for the lead carbonate a 31 per cent increase. These figures are based on the assumption that there is no migration of any of the products of decomposition.

The principle involved here is that metallic silver particles incased in either lead sulphate or lead carbonate are under enormous pressure and have these compounds so tightly "plastered" on their surfaces that liberation of a silver particle with a clean, metallic surface is an exception rather than a rule, especially in anglesite. Clean metallic silver particles, like gold, usually have irregular surfaces on which slime may easily accumulate to such an extent that the surfaces are entirely obscured. Soluble salts may tarnish the surfaces of otherwise clean metallic silver, so that they do not float readily. Thus, there are three tenable explanations for the tarnished or coated silver particles.

The studies on which the paper is based were made of products resulting from the treatment of ore that had been ground in a laboratory ball mill. The flotation tests were made by Mr. Zimmerley and extended over a period of several months.

Question 2. Sodium sulphide was used in making the tests and the silver particles in the concentrate had a slightly darkened color or tarnish, which, however, did not obscure their surfaces. It seems logical to suspect that such a tarnish might have been produced by the sodium sulphide. Fairly concentrated sodium sulphide solution is required to blacken a silver surface noticeably.

There was no evidence that silver particles in either the concentrate or tailing had surfaces abraded by attrition. As a matter of opinion, I am inclined to believe that the cleaning of gold and silver particles by attrition is limited to ores that are highly siliceous and virtually free from soft, slimy constituents. In the semioxidized ores, which usually contain an abundance of slime-forming minerals, there is a greater chance of surface contamination than there is of cleaning by attrition.

---

[5] G. L. Oldright and R. E. Head: The Microscope Reveals Influence of Mill Grinding on Floatability of Gold. *Eng. and Min. Jnl.* (June 1933).

# Oil-air Separation of Nonsulphide and Nonmetal Minerals

By Arthur F. Taggart* and G. R. M. del Giudice,* Members A.I.M.E.,
A. M. Sadler* and M. Hassialis*

(New York Meeting, February, 1938)

Flotation of sulphide minerals and native metals is no longer a practical difficulty. The underlying scientific principles of the method, although not explored in anything like complete detail, have been formulated with sufficient breadth so that the direction of attack on any specific case is clearly indicated. It has been known since the earliest days of flotation that certain of the nonsulphide nonmetal minerals—e.g., sulphur and graphite—would respond to flotation by oils as sulphides do; therefore they have been grouped with sulphides in many patents. But since the development of the chemical theory of collection,[1,2,3] this similarity in action has been one of the facts cited in disproof of the theory by opponents of the hypothesis.[4,5,6] Air levitation[†] of certain oxidized minerals, both metalliferous[‡] and nonmetalliferous, and separation thereby from other oxidized minerals, is a recent development in practice, although the discovery of the method dates back 17 years.[7] This paper presents evidence that the principles underlying the air levitation of the nonsulphide nonmetal minerals are the same as those utilized in the flotation of the sulphides and native metals.

It will be apparent immediately to anyone with knowledge of mineral concentration that separation of air-levitated minerals in water from minerals not so levitated is a simple matter of water-gravity concentration, the separating device employed depending solely upon the size of the particles treated and the buoyancy differences effected by the levitation. The usual separating means employed are: (1) a flotation machine for fine, slimy and for well aerated granular material; (2) shaking tables for granular less aerated material.

By using large quantities of oil, it is possible to form substantially air-free oil-bound masses or granules of nonsiliceous minerals and to

---

Manuscript received at the office of the Institute March 6, 1937. Issued as T.P. 838 in Mining Technology, September, 1937.

* Department of Mineral Dressing, Columbia University, New York, N. Y.

[1] References are at the end of the paper.

[†] The word "levitation" is used herein in the primary sense of rendering light. No definite extent of lightening is implied. Thus "air levitation" signifies lightening by means of air bubbles, and may denote either such a degree of lightening that the mineral will float in water, or such a lesser degree that simple flotation is impossible.

[‡] This word, as used herein, means "carrying a heavy metal."

separate these from unaffected siliceous minerals by hydraulic classification, the granules sinking. The principle of affecting the relative settling rates in water of the different mineral constituents of an ore utilized in this treatment are the same as those proposed by Cattermole[8] for sulphides and by Trent[8] for bituminous materials.

## Classification of Nonsulphide Nonmetal Minerals

On the basis of their behavior in oil-air separation, the nonsulphide nonmetal minerals may be separated into four classes, as follows:

1. Sulphur and the carbonaceous solids, graphite, anthracite, bituminous coal, the ozocerites and the like.
2. Oxidized metalliferous minerals.
3. Nonsiliceous oxidized minerals* of the alkalies and alkaline earths.
4. Siliceous minerals.

Definite separation of a mineral in any one of these four classes from the minerals of the other classes is theoretically possible, and the details of the separation have been worked out in a number of cases.

## General Principles of Separation

The method of oil-air separation involves broadly the selective air flocculation with consequent levitation of given minerals of groups 1, 2 and 3 above, with coincident nonlevitation of associated minerals of group 4, and subsequent separation of the levitated and nonlevitated individuals by suitable gravitational means. If separation is desired between minerals in groups 1, 2 and 3, conditions must be, and in general can be, so controlled as to produce levitation of minerals of one of the classes while the minerals of the other class are left unlevitated and dispersed. Ease of levitation usually is greatest for the minerals of group 1 and progressively less through groups 2 and 3. This is not to say that the minerals of group 1 have greater inherent floatability, but rather that they respond to a wider variety of collecting agents, or respond to a given collecting agent over a wider range of electrolyte concentration in the pulp.

The principle underlying selective levitation of minerals in groups 2 and 3 is the same as that utilized in flotation of sulphides; namely, coating with a hydrocarbon-like film by metathesis between an organic collecting agent and the substance of the mineral.[1] With the minerals in group 1, however, a different situation must exist, for the reason that metathesis between organic acids and these minerals is not chemically possible. The weight of the evidence, as will be immediately shown, is that with these minerals a collector of insoluble oily nature is necessary in order to obtain a water-repellent surface coating, and that the coating occurs because of solubility or a tendency theretowards of the mineral in the oil.

---

* The word siliceous is used herein to denote substances like or having the properties of quartz and other forms of silica, rather than in the broader sense of silica-containing. Essentially the properties comprised within the designation "siliceous" are relative insolubility in water and relative inertness toward chemical reaction, together with a content of silicon oxide. Under this usage certain silicates may and do appear in the nonsiliceous nonmetalliferous group (e.g., serpentine and talc), and certain others (for example, chrysocolla, garnierite, and even high-iron-bearing amphiboles such as hornblende) appear in the oxidized metalliferous group.

Gaudin[9] perpetuates the error of Sulman[10] and of a number of the early flotation patents[11,12] in ascribing what may be called inherent floatability to graphite and sulphur. Wark and Cox[5] fall into another error in respect to these minerals in that they assert that they are floatable by the use of collectors of the xanthate type. They go further and conclude from experimental evidence that convinces them of the truth of this assertion that this "fact" is evidence against the chemical theory of flotation.[6] The following experiments are directed toward testing the above assertions and toward development of the conclusions with respect to the actions of these minerals in flotation appearing in the preceding paragraph.

## SULPHUR

Sulphur is obtainable on the market in a wide variety of forms. For purposes of investigation the following varieties were obtained: natural sulphur crystals, recrystallized sulphur, roll sulphur, flowers of sulphur, precipitated sulphur, washed sulphur, and melted strip sulphur. The massive samples, comprising the two crystalline varieties and the roll sulphur, were polished by the method described in a paper by one of the authors.[13] It was impossible to produce on these materials a polished surface that would remain wet when removed from the polishing wheel. Since this is an invariable sign, so far as experience in the Columbia flotation laboratory is concerned, of an organic-contaminated surface, considerable time was spent in investigation as to the character and source of the organic contamination. In the first place, Ladoo[14] states that Texas and Louisiana sulphurs have a petroleum content ranging up to 0.2 per cent and that the average content is from 0.01 to 0.04 per cent. When an attempt is made to purify such sulphur either by sublimation or by evaporation from organic solvents, more or less of this petroleum content will go with the sulphur. Subsequent heating of sublimed sulphur to the melting point for casting into rolls is insufficient to drive off petroleum. Since Texas and Louisiana supply most of our domestic sulphur, this contamination must always be expected in sulphur of unknown origin. When "recrystallized sulphur" was ground in a mortar, a strong odor of carbon bisulphide was noticed. Carbon bisulphide is an excellent collector for sulphur. Attempt was made to remove the carbon bisulphide, which inquiry developed was the solvent from which the specimen had been recrystallized, by melting the material. Melting in the atmosphere and heating almost to the point of ignition for several hours was insufficient to drive off the solvent, as was evidenced by the fact that upon cooling and solidification and subsequent pulverization in a mortar, an odor of carbon bisulphide was again distinguishable. The odor was much diminished, however, and this material yielded polished surfaces to which air bubbles clung but slightly in the bubble machine[1] in clean tap water. A sample of flowers of sulphur was dissolved in benzene and recrystallized therefrom in the hope that with the lighter solvent it would be easier to drive off the last traces by heating. This could not be done, however, by heating in the atmosphere, nor by partial distillation under low vacuum (about 10 mm. of mercury). An approach to freedom from organic contamination was made by twice recrystallizing C. P. crystalline sulphur from thiophene-free benzene and thereafter passing nitrogen through the molten recrystallized product at 135° C., first at atmospheric pressure and thereafter at reduced pressure for 1½ hr. The sample was thereupon permitted to solidify, and upon polishing showed no adherence after 30 sec. pressure contact with an air bubble, but did show a slight clinging after 2 min. pressure contact.*

The other forms of sulphur mentioned above, when cast into small ingots and polished, gave much cleaner surfaces than any of the originally massive forms, but were not completely uncontaminated. Ingots from melted strip sulphur were so far superior, as originally made, to those made from other forms of sulphur, however, that this material was adopted as the best material for our tests. Certain batches of this material when cast into ingots and polished gave surfaces that were wet completely after polishing on clean felt on an aluminum wheel.

With neither of the clean sulphurs described above would air make contact in clean tap water. Nujol (a mixture of hydrocarbons of the paraffin and napthene types, extensively purified by acid, alkali and water washes) makes ready contact and gives an apparent equilibrium contact angle of the order of 80°.† Upon further withdrawal of the bubble holder the contacting droplet necks off, leaving a residue on the surface of the sulphur that assumes a position such that the apparent contact angle measured through the water is 130° to 140°. Substantially the same results were obtained when a highly purified hydrogenated naphtha of substantially kerosene boiling range was substituted for Nujol; also with a laboratory redistilled kerosene that had stood on the shelves for some three or four years and become somewhat discolored and had deposited a certain amount of gum; and also with 10 per cent solutions of oleic acid in Nujol and in the hydrogenated naphtha. These same sulphurs, when conditioned 5 min. in a temporary emulsion of Nujol in tap water (1 part in 8000) and then transferred to tap water in the bubble-machine cell, showed a contact angle with air of 85°; after similar conditioning in an oleic acid emulsion of the same concentration the air-contact angle was 60°. On the other hand, conditioning for the same time in a solution of potassium ethyl xanthate (25 mg. per liter) gave zero contact with air, but after conditioning in sodium oleate solution (25 mg. per liter concentration, pH about 9) air made immediate contact with a 74° angle in clean tap water.

---

* Pressure contact means pressing the bubble against the particle surface by means of the bubble holder, with sufficient force to deform the bubble to such an extent that any further pressure would cause the bubble to squeeze out of the holder and escape.

† An equilibrium contact angle is obtained by first pressing the bubble against the solid surface, then backing off the holder until the projection of the contact circle first begins to shorten, then tapping the cell with sufficient force to cause the bubble to wabble vigorously.

The oil results just cited indicate that hydrocarbons, both purified and when containing acidic constituents, displace water readily from the surface of sulphur, and so film and condition the surface that it thereupon becomes water-repellent in the presence of air, and consequently will attach air bubbles and can be floated. Potassium ethyl xanthate does not produce a water-repellent surface on clean sulphur. The experiment with soap is properly to be interpreted not as an indication of adsorption of sodium oleate, but that the sulphur is oiled with oleic acid. The pH of the soap solution indicates hydrolysis of the soap, a reaction that results in the production of a certain amount of free oleic acid.[15,16] The contact angle of air against this soap-conditioned surface is roughly the same as that obtained by conditioning with a dilute emulsion of oleic acid. The discrepancy, which exceeds the expectable error of the apparatus, may be attributed to the much finer dispersion of the oleic acid precipitated by hydrolysis.

The mechanism by which the surface of the sulphur is conditioned by oils may be looked upon as one of mutual solution of the sulphur and oil. The sulphur surface is visibly etched when a drop of oil is placed upon it and subsequently washed away. Powdered sulphur readily dissolves, in small concentrations, in Nujol and in hydrogenated naphtha. When a sulphur particle with a polished surface about 1 cm. wide and 2.5 cm. long that has been touched by a Nujol droplet about 2 mm. in diameter is removed from the cell, an etched circle about 2 mm. in diameter is plainly marked on the surface, and the remainder of the surface, which was not water-repellent before immersion in the tap water in which Nujol contact was made and into which no reagent other than Nujol had been introduced, is now highly water-repellent. This we take to indicate that a film of the Nujol has extended, by reason of its solubility in the sulphur, over the entire surface, and that the contact angle measured for the residual droplet of Nujol on this surface is actually a three-phase angle between a substantially monomolecular film of the Nujol at the solid surface, mass Nujol, and mass water. The phenomenon is similar to the heaping up of oleic acid or of Nujol contaminated with oleic acid at the air surface of water when an amount of oil in excess of that required for a film of relatively few molecules thick is placed on the water.

The failure of potassium ethyl xanthate to activate clean sulphur, recorded above, is in line with the failure of amyl xanthate to cause air-bubble contact with sulphur, as recorded by Wark and Cox. These experimenters state, however, that high concentrations of di-*n*-butyl dithiocarbamate (500 mg. per liter or 40 times the usual flotation concentrations) did cause contact. We confirmed the latter observation to the extent that we obtained a contact angle of 60° with sulphur after 5-min. conditioning in a 200-mg. per liter solution of sodium di-ethyl dithiocarbamate. On the other hand, as will be developed in detail in discussing the behavior of graphite, we believe that this contact was due to an oily decomposition product of the carbamate, and not to molecular adsorption thereof.

Wark and Cox cite, as further evidence of adsorption of xanthate-type collectors by sulphur, experiments in which amyl xanthate solutions shaken with flowers of sulphur lose xanthate. In their tests 2 grams of flowers of sulphur were contacted with 16 c.c. of xanthate solutions of varying concentrations for a period of 3 hr., then filtered off and the filtrate tested for xanthate. We confirm their experimental fact as to loss of xanthate under such circumstances, using ethyl xanthate (Table 1); but this is true only for sublimed sulphur and, to a much less extent, for natural sulphur. The explanation for the disappearance of xanthate ion with these products is the presence of sulphuric acid therein. Aqueous extracts of Eimer and Amend flowers of sulphur (using 10 parts $H_2O$ to one of S) after 3 hr. contact show a pH of 2.0 colorimetrically and 2.2 with the hydrogen electrode; a heavy precipitate with $BaCl_2$ solution; and analyze 24 mg. $H_2SO_4$ per 100 c.c. by titration to phenolphthalein pink with NaOH, and 21.9 mg. $SO_4^=$ per 100 c.c. by the $BaSO_4$ gravimetric method. Dilute sulphuric acid solutions precipitate xanthic acid from its alkali salts and this acid decomposes rapidly in water at normal temperatures. In test 14 (Table 1) the original solution and the filtrate were tested for potassium, with the result that 27.2 mg. $K_2SO_4$ per 50 c.c. was found in both. In tests 17 and 18 is found confirmation of the effect of sublimation. A sample of E. and A. crystallized sulphur recrystallized twice from benzene was sublimed in a glass retort and the sublimate and pulverized residue were then treated with xanthate solution as shown in the table. This sulphur had no effect on xanthate solution before sublimation (tests 9, 10) and the residue showed no effect (test 18) but the acidic sublimate caused the decomposition of 71.6 per cent of the xanthate ion originally present.

TABLE 1.—*Extent of Decomposition of Potassium Ethyl Xanthate Solutions by Sulphur*

| Test No. | Variety of Sulphur | Concentration of Solution Mg. KEtX per Liter | Time of Contact | | Loss of KEtX | | pH of Filtrate |
|---|---|---|---|---|---|---|---|
| | | | Min. | Hr. | Per Cent | Mg. per Gram S | |
| 1 | Roll | 500 | 15 | | 2.2 | 0.11 | 7.0 |
| 2 | Precipitated | 500 | 60 | | 0 | 0 | 7.0 |
| 3 | Precipitated | 500 | 15 | | 0 | 0 | 7.4 |
| 4 | Washed | 500 | 60 | | 0 | 0 | 7.0 |
| 5 | Natural, crystalline | 500 | 15 | | 23.2 | 1.16 | 7.4 |
| 6 | Strip | 500 | 15 | | 2.3 | 0.12 | 7.2 |
| 7 | Strip | 500 | 60 | | 0.6 | 0.03 | 7.2 |
| 8 | Recrystallized from $CS_2$(E. & A.) | 500 | 15 | | 0.3 | 0.01 | 7.4 |
| 9 | Recrystallized from $C_6H_6$[a] | 500 | 15 | | 0 | 0 | |
| 10 | Recrystallized from $C_6H_6$[a] | 1024 | 30 | | 0 | 0 | 7.4 |
| 11 | Flowers (E. & A.) | 500 | 15 | | 98.4 | 4.9 | 4.5 |
| 12 | Flowers (E. & A.) | 1024 | 60 | | 55 | 5.6 | 7.2 |
| 13 | Flowers (E. & A.) | 1024 | | 3 | 74 | 7.6 | |
| 14 | Flowers (E. & A.) | 1024 | | 51 | 78.5 | 8.1 | |
| 15 | Flowers (Col. U. Chem. Stores) | 200 | | 3 | 100 | | |
| 16 | Flowers (Col. U. Chem. Stores) | 1000 | 60 | | 74 | 7.6 | 7.2 |
| 17 | Sublimate of 9 above | 1000 | 30 | | 71.6 | 14.7 | 6.4 |
| 18 | Residue from sublimation of 9 | 1000 | | 16 | 0 | 0 | 7.4 |

[a] This is the same sulphur as 8, which is described on page 183.

The other tests shown in Table 1 demonstrate that with varieties of sulphur that are not acid the destruction of xanthate ranges from nil to negligible.

Potassium di-n-ethyl dithiocarbamate shows no loss when 10 parts of a 250-mg. per liter solution is shaken with one part of pulverized strip sulphur.

Test-tube flotation tests with strip sulphur pulverized under water in a porcelain mortar showed about ½ in. of froth with no measurable diminution of settled solid when no reagent was present. Tests in which were added respectively 30 mg. per liter of iso-amyl alcohol, the same amount of alcohol plus 5 mg. per liter of potassium amyl xanthate, and the alcohol plus 10 mg. per liter of potassium di-ethyl dithiocarbamate all showed about ½ in. of froth carrying roughly 80 per cent of the sulphur. These tests indicate, as was to have been expected from the results shown in Table 1, that the soluble collectors have no effect on the flotation of sulphur when the conditions are not such as to break the collector down into oily decomposition products. If the pulp is acid, the xanthate-salt type of collectors decompose into relatively insoluble oily acids, alkyl sulphides and disulphides, and finally to $CS_2$, all of which may be expected to float sulphur as they float graphite (see p. 189).

These experiments would seem to demonstrate conclusively that the xanthate-type collectors neither react with nor adsorb on sulphur surfaces, and, when present as such, have no effect on either air-bubble contact with sulphur or flotation thereof.

## GRAPHITE

Graphite proved harder to purify than did sulphur. Dixon's Perfected American Graphite for Electrotyping, No. 649, was shaken intermittently for 1 hr. with 10 times its weight of potassium ethyl xanthate solution (200 mg. per liter). The filtrate contained only 3.5 per cent of the original xanthate. One-half hour's shaking in KEtX solution of 500 mg. per liter concentration left 19 per cent of the xanthate in the solution. This same graphite was then heated for 15 min. to red heat in a porcelain crucible, and, after cooling, shaken 35 min. with 10 times its weight of KEtX solution (500 mg. per liter). The filtrate now contained 57 per cent of the original xanthate. The heated graphite was next acid-purified by washing for 10 min. in 1:1 HCl, followed by 1:3 HCl, then 1:9 HCl and then distilled water. There was a strong odor of $H_2S$ when the concentrated acid was applied. The combined filtrate from the first two acid washes was yellow and gave a strong test for iron. The acid-washed sample, after shaking 15 min. with 10 times its weight of KEtX solution (500 mg. per liter) left 65 per cent of the xanthate in the filtrate. After being heated for 15 min. at red heat, the acid-washed sample left 75 per cent of the xanthate unaffected. Further treatment by washing with two successive nitric acid washes (20 per cent $HNO_3$) and 15 min. ignition reduced the xanthate removal to 21 per cent. It is clear from these tests that this graphite was impure and that the impurity, which was progressively though never completely removed by the acid and heat-treatments was, in part at least, responsible for the xanthate removal.

Some light on the character of this removal is to be found in the fact that a xanthate solution (500 mg. per liter) after 15 min. shaking with the treated graphite gave a pH of 9.4, while the pH of a water extract of the same graphite is 7.4. Unless it is assumed that the graphite in some way furnishes carbonate ion, this increase in alkalinity can result only from decomposition of the xanthate, of such a nature that insoluble decomposition products of the sulphide type are formed, thus freeing alkali metal ion with consequent increase in hydroxyl-ion concentration.

Acheson graphite No. 38 (described as "Unctuous Acheson Graphite, Grade No. 38. Guaranteed 99.9 per cent pure graphitic C. A soft, unctuous, extremely fine amorphous powder. Made in the electric furnace at a temperature over 7500° F.") when tested as purchased, caused 12.5 per cent reduction in the xanthate content of a KEtX solution of 500 mg. per liter concentration. Degassing of this graphite at

100° C. for 4 hr. at 1 mm. pressure reduced the xanthate consumption slightly. The pH of the filtrate from the treatment of degassed material was 9.0, indicating, as noted in the preceding paragraph, decomposition to sulphides.

On inquiry, the research laboratory of the National Carbide and Carbon Co. furnished us with specially purified graphite both in powder and stick form (compressed without a binder). Two grams of the powder shaken 1 hr. with 20 c.c. of KEtX solution (200 mg. per liter) caused a 40 per cent loss of xanthate. A faint odor of $H_2S$ during the first part of the hour's shaking and of $CS_2$ toward the end, coupled with a rise in pH from 7.2 to 9.0 during the same time, indicates that the loss was due to sulphide-producing decomposition. When this variety of graphite was heated to red heat for 10 min. and, after cooling, again treated with xanthate solution as above, the loss of xanthate was reduced to 26 per cent. The pH of the treated solution was again 9.0.

Potassium iso-amyl xanthate solution (approximately 500 mg. per liter, but exact concentration unknown) lost about 60 per cent of its strength after 3-hr. contact with National Carbon graphite. The pH rose from 8.0 to +9.8. The normal amyl xanthate did not change solution concentration (500 mg. per liter) on 3-hr. contact, but the pH fell from 9.4 to 7.6.

The conjecture that the loss of xanthate caused by graphite is due to decomposition of the xanthate to sulphides is partly substantiated by the fact that when the treated graphite is extracted with ethyl ether, the ether yields on evaporation a considerable quantity of oily residue that smells like impure dixanthogen or carbon bisulphide.

An attempt to support a conjecture that the decomposition of xanthate by purified graphite is due to oxidation by oxygen held by the graphite was partly successful. Graphite boiled in water for 15 min. and sealed in the hot water was treated, when cooled, in the resulting partial vacuum with KEtX solution (20 mg. per liter).* The consumption of xanthate was 25 per cent of that added. This compares with the 40 per cent consumption noted above when treatment of unboiled graphite was effected in air. Since the decomposition of xanthate solution of this strength is only about 3 per cent on standing two days in air, it may be inferred that a part of the difference, at least, is due to the boiling of the graphite.

Air-bubble contact-angle tests against the National Carbide Co. stick graphite in solutions of 200 mg. per liter concentration gave no contact after conditioning for 5 min. with potassium ethyl xanthate, potassium di-ethyl dithiocarbamate, or potassium n-amyl xanthate. The same was true after conditioning for 1 hr. in the carbamate solution and after 24 hr. in the xanthate solutions. In two cases the pH of the solution rose. (Carbamate: original solution, 7.4; after 5 min., 8.6; after 1 hr, 9.0. Ethyl xanthate: original solution, 7.2; after 5 min., 8.2; after 24 hr., 9.2.) Hydrogen-ion concentration was not measured in the amyl xanthate solutions.

---

* Oxygen dissolved as air in 25 c.c. of a solution of KEtX of 800 mg. per liter concentration added to 75 c.c. of boiled water in the flask to bring the concentration up to this figure was present with the 10 grams of boiled graphite tested.

TABLE 2.—*Flotation Tests on Graphite*

| Test | Reagents | | Result |
|---|---|---|---|
| | Name | Mg. per Liter | |
| 1 | None | | Flocculation. Slight surface film. |
| 2 | Terpineol | 10 | Flocculation. About ¼ in. froth but no substantial fraction of the total solid floated. |
| 3 | Terpineol | 40 | |
| 4 | Iso-amyl alcohol | 30 | |
| 5 | Iso-amyl alcohol | 300 | Not appreciably different from 2. |
| 6 | Acetone | 10,000 | |
| 7 | Acetone | 10,000 | |
| | Potassium n-amyl xanthate | 5 | |
| 8 | Iso-amyl alcohol | 30 | |
| | KEtX | 25 | |
| 9 | Iso-amyl alcohol | 30 | |
| | KEtX | 200 | |
| 10 | Iso-amyl alcohol | 30 | |
| | K n-Am X | 5 | |
| 11 | Iso-amyl alcohol | 30 | |
| | Na di-butyl dithiocarbamate | 10 | |
| 12 | Iso-Am OH | 30 | |
| | Kerosene | 1 drop | All floats |
| 13 | Iso-Am OH | 30 | |
| | $CS_2$ | 1 drop | All floats |
| 14 | Iso-Am OH | 30 | |
| | Ethyl dixanthogen | 30 | No flotation cold but good flotation at 30° to 40° C. |

Flotation tests with the National Carbon graphite, paralleling those of Wark and Cox,[5] are shown in Table 2. All of the tests were made in 30-c.c. test tubes with 1 gram of solid and 15 c.c. of liquid. The tubes were closed with clean corks and shaken vigorously 100 times. These tests show definite failure on the part of soluble collectors to float reasonably pure graphite, and high activating efficiency on the part of oily substances, two of which [$CS_2$ and $(C_2H_5O.CS.S)_2$] are xanthate decomposition products.

## OILING OF CARBONACEOUS MATERIALS

Significant results bearing on the general behavior of the substances of group 1 were obtained by experiments on polished surfaces of the following series of solids: paraffin wax, gilsonite, a bituminous coal of medium volatility, anthracite, and the National Carbide Co. stick carbon. In clean tap water, air made contact angles of 104° with the paraffin and of 75° with the gilsonite, gave a slight clinging contact of no definitely measurable angle* with the bituminous coal, and a zero angle, which is to say, no contact, with the anthracite and carbon. None of these air contact angles is affected by preconditioning of the solid in potassium ethyl xanthate solution. All oils tested, comprising purified and impure petroleum hydrocarbons, oleic acid, mixtures of oleic acid with purified hydrocarbons, and coal-tar creosote, made immediate contact with all of the surfaces, giving an equilibrium contact angle of about 80° and a residual droplet contact angle (see p. 183) of upwards of 160°. All produced etch circles on the polished surfaces at the spots of contact therewith, the severity of the etching decreasing regularly throughout the series from paraffin to purified carbon, and ranging from relatively deep pitting on the paraffin to an almost indistinguishable change in luster of the purified carbon surface. Conditioning in potassium ethyl xanthate solution had no effect, so far as air-bubble contact was concerned, on bituminous coal and anthracite. Conditioning in sodium oleate solution and in emulsions of Nujol and of oleic acid in water rendered both bituminous coal and anthracite water-repellent.

The indication of these tests is that, as with sulphide minerals, the surface must be of a hydrocarbon nature for air-bubble contact to occur, and further that the nature of the hydrocarbon must be such that the carbon-hydrogen ratio is relatively near that present in the normal petroleum hydrocarbons. This surface is already naturally present in paraffin and gilsonite. In the bituminous coal the hydrogen-carbon ratio is well below that present in petroleum hydrocarbons, and in anthracite tremendously below. However, in these minerals and the purified carbon it is readily produced by contact with dispersed oil droplets in the presence of water, and the mechanism of such production is mutual solubility of the solid and of the oil. Soluble collectors of the xanthate type do not produce the coating.

The solution theory of oiling by nonreactive oils as set forth above is further substantiated by the facts given in a previous paper in which two of the authors of this paper collaborated (ref. 3, p. 360), wherein it was shown that hydrocarbon oils would coat sulphide surfaces and those of the minerals of groups 2 and 3 of this paper only when those surfaces were so conditioned as to present to the hydrocarbon a surface soluble therein.

---

* This clinging contact is so weak that when the cell is tapped to obtain an equilibrium contact angle, as previously described, the bubble will not cling but peels away and assumes a position determined by the downward pressure of the bubble holder, the buoyant effect of the water in the cell and upward pressure of the polished surface.

Further evidence of the same nature is presented by an experiment in which a crystal of $CuSO_4.5H_2O$, which is readily soluble in water, is polished in purified naphtha and the polished surface exposed in purified naphtha to a bubble (drop) of water. Under these circumstances the water bubble readily displaces the naphtha from the surface of the copper sulphate over a restricted area, forming a definite contact angle, in the same way precisely that oil displaces water at the surface of an oil-soluble water-insoluble substance such as paraffin, and after removal from the bubble machine the particle surface is seen to be etched.

In the light of the tests herein set forth, we are unimpressed by the Wark and Cox criticism of the theory of metathesis of chemical collectors in sulphide-mineral flotation, based by them on the actions of sulphur and graphite with xanthate-type collectors, as expressed in two of their recent papers. We feel that molecular adsorption of the alkali collector salts by group 1 minerals, asserted by them to occur, is definitely disproved both by our showing that potassium is not removed from xanthate solution by contact with sulphur, and by the critics' own experiment[5] on graphite showing no abstraction of xanthate ion from graphite coated (according to them) with adsorbed alkali ethyl xanthate, when the "coated" graphite is washed in warm fresh water. If their graphite had been so coated, there must have been partition of the adsorbed layer between the adsorbing surface and the wash water, in accord with well established principles of colloidal chemistry. We feel that the data, both those presented by Wark and Cox and our own, point to the conclusion that the minerals of our group 1 are activated only by oils in which they tend to be soluble, and that the only way in which xanthate-type collectors can affect their activation is by decomposition to produce such oils.

## Oxidized Nonsiliceous Minerals

Practice in the oil-air separation of oxidized nonsiliceous minerals (groups 2 and 3) has demonstrated that the use of oil mixtures containing both nonreactive hydrocarbons and a reactive (acidic) oil, or preconditioning with a reactive collector such as sodium oleate and subsequent oiling with a hydrocarbon oil, give better results than the use of a reactive oil (oleic acid) alone or of a soluble collector (e.g., an alkaline oleate) alone. The reason for this probably lies in the fact that the reaction of soluble collectors with the oxidized nonsiliceous minerals is, in general, much more deep seated than the oxidation reaction with freshly broken sulphide minerals in the ordinary mill pulp, with the result that the layer of reaction product with the collector is of more than monomolecular thickness, and that the molecules are not, therefore, like-oriented. Gas-bubble attachment to such "massive" surfaces is not ready, but hydrocarbon oils wet them freely, and gas attachment to the hydrocarbon films is quick and tenacious.

In general, the reactive collecting agent for minerals of groups 2 and 3 contains or supplies in the pulp an organic acid radical. The most important of the organic acid radicals known to be useful for oil-air separation of these minerals are those of the higher fatty acids, both of the saturated and oleic series, and the resin acids. The characteristic ions of these acids form relatively insoluble salts (soaps) when combined with heavy-metal and earth-metal ions, and they are readily dispersed in water in controlled and controllable quantities, by the use of alkalies. The lower acids of these series have but little effect. Thus valerianic acid dissolved in hydrogenated naphtha causes the naphtha to barely cling to apatite, although with malachite a small residual droplet is left on the surface as the oil is pulled away. It is interesting to note, however, that Barrett No. 4 coal-tar creosote, which, although a complex mixture of acidic and basic constituents in dissolved hydrocarbons, has a relatively low content of fatty acid, has much the same oil-coating effect on apatite and malachite in bubble-machine tests as on sphalerite and galena.

## Hydrogen-ion Concentration

The metallic soaps differ among themselves in the ranges of hydrogen-ion concentration through which they can form and persist. Thus heavy-metal soaps, such as lead, copper, and zinc, will form and are stable in pulps of hydrogen-ion concentration as high as is indicated by a pH of upwards of 3 or 4, and oxidized minerals of these metals could, therefore, be coated in pulps of these acid concentrations were there any necessity to so operate. On the other hand, calcium soaps will not form and are unstable in hydrogen-ion concentrations greater than those indicated by pH 7, and for this reason calcium minerals require to be coated in pulps with a pH range on the alkaline side of chemical neutrality.

Excess of alkali results in the formation of a soapy nonselective froth with both metalliferous and nonmetalliferous oxidized minerals. The point at which this overfrothing condition occurs is at a pH between 9 and 10 with oleic acid, and is near this with other fatty acids, unless some provision is made to retard soap formation, as by adding oleate ion in the form of oleic acid dissolved in an insoluble oil like petroleum. Under these circumstances the partition of oleic acid between oil and water so greatly favors the oil that reaction between hydroxyl ion and the hydrogen ion of the acids to free oleate ion is limited to the interface between the oil droplets and the water, and the appearance of oleic acid molecules at the oil-water interface is necessarily limited in rate by the diffusion rate of the oleic acid through the unstirred petroleum droplets.

The result is that the formation of soluble soap, which is the frothing agent responsible for the nonselective foam that characterizes undue alkalinity, is materially suppressed, and oleate ion as formed at the surface is freed into the water as such, and as such enters into the coating metathesis with the mineral surface. Excessive alkali does not, on the other hand, prevent the coating reaction from occurring. Thus polished surfaces of both malachite and apatite conditioned in sodium oleate solutions of 125 mg. per liter, of pH = 11.97, although they show no air-bubble contact in the soap solution itself, and thereby parallel the action of the ground minerals in a flotation cell, give characteristic oleate contact angles (60°) when wiped and thereafter tested in plain water. Similarly, in a batch-flotation cell with phosphate rock, if the soapy froth is removed, the pH of the pulp drops, and when soluble soap and alkali concentration have fallen sufficiently, the phosphate mineral-air agglomerates float.

## Salts

Neutral salts in high concentrations also tend to prevent effective oil coating and levitation of nonmetalliferous oxidized minerals.

## Elements of Operation

There are three elements of operation peculiar to the levitation of the nonmetallic minerals of groups 2 and 3 as compared with the levitation of the metallic minerals; namely: (1) the quantity of reagent required; (2) the possibility of interference with selective levitation by iron, and, to a lesser extent, by others of the heavy metals; and (3) the controlling influence of certain slimes.

### *Quantity of Reagent*

The quantity of reagent necessary in the flotation of nonmetallic minerals is controlled by the same relations that hold in the treatment of metallic minerals; namely: (1) the dependence on surface to be covered, which in turn is determined by the quantity of mineral that is to constitute concentrate, the size to which this mineral is ground, and the depth to which the reaction proceeds; (2) the density of the pulp, which controls the spacing of the particles to be oiled; (3) the temperature of the pulp, which has a controlling influence on the degree of dispersion of the coating oil; and (4) the hydrogen-ion concentration of the pulp, which likewise affects the degree of dispersion of the coating oil, and also, as previously noted, the number of free organic-acid ions. But even allowing for the fact that the nonmetallic ores contain in general a larger percentage of mineral to be concentrated than do the metallic ores, there yet seems to be the necessity, in general, for relatively larger quantities of collector than is usual in metallic-mineral practice. Thus, operation in the Florida phosphate field on pulps that range in size from 14 or 20-mesh to 100-mesh, with substantially no minus 100-mesh material, a minimum of 4 to 5 lb. of oil per ton of ore seems to be necessary, about one-quarter of this amount being fatty acid. The proportion both of reactable collector (the fatty acid) and smearing oil (the petroleum) in this practice per unit of area of phosphate mineral is markedly higher than that of xanthate plus the undissolved fraction of a pine-oil frother, for example, in any sulphide flotation practice with which the writers are acquainted.

A part of the explanation for this difference lies in the fact previously noted that no smearing oil is necessary with sulphides. But this is certainly not all. A hint of explanation is to be found in the fact that the quantity of oil required increases tremendously with relatively small traces of slime present in phosphate ores, and the further fact that, in the presence of such slime, oil droplets taken from a pulp undergoing treatment are rather heavily slime-coated at the oil-water interface. If we may accept this observation at its face value, it means that oil thus coated is mechanically prevented from making effective smearing contact with the concentrate mineral, and hence is substantially inert in the process. If this is the proper explanation, it is apparent that concentrate mineral slime would be even more effective than clay slime in inhibiting the smearing action of the oil, for the reason that reaction between these slimes and the oil, resulting in oil-coating of the contacting surface and consequent stability of the slime particle in the oil-water interface, is of the *modus operandi* of the process.

On the other hand, practice at the Valley Forge Cement Co., where the calcite in a crudely deslimed calcite-mica-quartz pulp, substantially all passing 80-mesh and of which a large part is minus 325-mesh, is floated with between ½ and ¾ lb. of fatty acid per ton of feed, gives promise that there is no fundamental necessity for so great a discrepancy in collector quantities between nonmetallic and metallic-mineral operations.

### *Iron*

The effect of iron, and, to a lesser extent, of certain other heavy metals, is to activate siliceous minerals to such a degree that they tend to become oiled and levitate with nonsiliceous minerals. The nature of the activating action is not as yet completely explored. The following facts have been observed:

1. If relatively fine iron filings in the very considerable proportions of 2 grams of iron per 15 grams of minus 48 plus 100-mesh quartz are shaken with 50 c.c. of water in a test tube with free access of air, or are vigorously stirred in a beaker open to the atmosphere, the water becomes colored brown in a very short time, and the brown tint increases rather

rapidly so that in 15 min. it is a light chocolate color. If the quartz after such stirring is washed and the residual metallic iron in the mixture is removed before drying, there is no visible tint on the quartz after 1-min. stirring, but from 3-min. stirring upward there is an increasing visible yellow-brown discoloration. The discolored quartz can be air-flocculated, using oleic acid (5 lb. per ton) in pulps ranging from pH 4.5 to pH 9. (These are the limits of experimentation rather than the limits of air-flocculation.) The quartz that was agitated with iron for 1 min. and not visibly stained does not air-flocculate.

2. Similar activation of the quartz occurs with ferric hydroxy sol.

3. Ferric chloride solution activates quartz without visible staining.

4. A polished surface of quartz activated by stirring for 15 min. in the presence of iron filings gives air-bubble contact after conditioning with sodium oleate solution, and shows under the microscope, at 500 diameters magnification, scattered patches of a brownish material that is of the same color as the precipitate formed by mixing a solution of ferric iron with a solution of sodium silicate.

5. Quartz polished on felt with magnesia powder, the felt being mounted on a bronze wheel and kept wet with tap water, which, although perfectly clear to the eye showed on filtration considerable quantities of iron rust, gave a contact angle when conditioned with sodium oleate. This quartz surface showed no visible traces of staining under the microscope. When new polishing felt was used with distilled water on the wheel, no contact angle developed after conditioning with sodium oleate.

The experiments described above indicate that the activating reaction with iron involves metathesis between ferric ion and silicate ion to form a deposit of a ferric silicate at the quartz surfaces. Activation without staining by ferric chloride, and failure to activate without staining in the case of metallic iron indicates that when the ferric ion is present in ferric hydroxide, actual contact of the relatively insoluble hydroxide particles with the quartz is necessary.

As might be expected, any method for lessening the concentration of ferric ion in the pulp or of increasing the size of ferric hydroxide aggregates, or which tends to prevent the formation of ferric silicates, tends to prevent the activating effect of iron. The high-acid pulps used in early sulphide flotation, when oleic acid and oleic acid-petroleum mixtures were used as collectors, served the purpose of preventing the formation of ferric silicate by suppressing silicate ion. Phosphate ores introduce phosphate ion into the pulp, which reacts with ferric ion to form relatively insoluble ferric phosphate, and in that way to prevent iron activation of quartz. Operation in alkaline pulps tends to aggregate ferric hydroxide around the particles of metallic iron and thus, both by a protective coat and by gelatinization, prevent harmful dispersion.

Failing any of these protective means or their equivalents, it probably will be necessary in the separation from quartz of minerals that are difficultly soluble and consequently difficult to air-flocculate to eliminate iron by grinding out the presence of iron.

### *Slime*

With certain ores, of which the Florida phosphates are a notable example, the presence of slime in the pulp has a marked effect on the levitation of the ore minerals. Not only does the slime increase greatly the quantity of oil necessary to effect levitation, but also levitation of the coarser mineral is deferred until a considerable part of the slime (both that of the concentrate mineral and the gangue) has been removed. Examination of polished surfaces of the phosphate rock shows that the phosphate particles in the pulp are heavily slime-coated unless a suitable electrolyte is added. Sodium hydroxide reduces the slime coating materially. Soap (sodium oleate) makes a nonselective slimy froth in the early part of an operation with slime-bearing pulps. After this is removed, flotation of the residual coarser mineral can be effected. On the other hand, apatite from igneous rocks and malachite in quartzitic ores are readily floated in slime-bearing pulps.

The remedy for slime interference is simple in the Florida phosphate practice. The slimes, which are relatively worthless clay in most cases, are removed by overflow and thrown away. At the Valley Forge Cement Co. the flotation feed is deslimed and the slime recombined with the concentrate. Where neither of these methods is available to an operator and the ore contains a harmful slime, some special method of handling will have to be devised. If, as is to be suspected in the light of the research of one of the authors,[17] the slime coating reaction is one that involves metathesis between the slime and the valuable mineral, resulting in the production of a cement that holds the particles together, the nature of the method may be readily predicted, although the detail of working it out may yet present considerable difficulty. Thus the necessary procedure will involve introduction of a reagent that will render either the mineral surface or the slime-particle surface too insoluble to enter into the reaction to produce the cementing material, or else the added reagent must prevent formation of the cementing reaction product.

## BIBLIOGRAPHY

1. Taggart, Taylor and Ince: *Trans.* A.I.M.E. (1930) **87**, 285.
2. Taggart, Taylor and Knoll: *Trans.* A.I.M.E. (1930) **87**, 217.
3. Taggart, del Giudice and Ziehl: *Trans.* A.I.M.E. (1934) **112**, 348.
4. Wark and Cox: *Jnl. Phys. Chem.* (1933) **37**, 797.
5. Wark and Cox: *Jnl. Phys. Chem.* (1935) **39**, 551.
6. Wark and Cox: Page 26, this volume.
7. N. C. Christensen: U. S. Pat. 1467354.

8. Taggart: Handbook of Ore Dressing, 945. New York and London, 1927. John Wiley & Sons and Chapman & Hall.
9. Gaudin: Flotation, 38, 342. New York, 1932. McGraw-Hill Book Co.
10. Sulman: *Trans.* A.I.M.E. (1919) **29,** 44.
11. Cattermole, Sulman and Picard: U. S. Pat. 788247.
12. Sulman, Picard and Ballot: U. S. Pat. 835120.
13. del Giudice: *Eng. and Min. Jnl.* (1936) **137,** 291.
14. Ladoo: Non-metallic Minerals, 612. New York, 1925. McGraw-Hill Book Co.
15. McBain and Martin: *Jnl.* Chem. Soc. (1914) **105,** 957.
16. McBain and Jenkins: *Jnl.* Chem. Soc. (1922) **121,** 2325.
17. del Giudice: *Trans.* A.I.M.E. (1934) **112,** 398.

## DISCUSSION

(*Arthur F. Taggart presiding*)

R. Schuhmann, Jr.,* Cambridge, Mass. (written discussion).—The authors recognize the inapplicability of the "chemical theory" of collector action—namely, coating by metathesis, as stated on page 181—to the collection of nonsulphide nonmetal minerals of class 1 (sulphur, carbonaceous solids, etc.). On the basis of a general parallelism, they then advance "the solution theory of oiling by nonreactive oils," stating that a water-repellent coating is formed on the surfaces of minerals of this class "*because of* solubility or a tendency theretowards of the mineral in the oil." Later, this is extended further, "the *mechanism* of such production [of a hydrocarbon surface of proper carbon-hydrogen ratio] is mutual solubility of the solid and of the oil." [Italics and brackets mine.] Solubility is defined as a quality or state, or as a quantity, and is not in any sense a mechanism; hence we can continue discussion only by assuming that the intended mechanism is mutual solution.

The authors of the solution-oiling theory have demonstrated a parallelism for certain cases between mutual solubility and the tendency for oiling to take place, and have shown that both mutual solution and oiling do take place to some extent simultaneously; they conclude that solubility [solution] is the mechanism of the oiling. The simple statement of the parallelism for certain cases is just as valuable to us in a practical way and is an experimental fact; furthermore, such statement implies that both mutual solution and oiling are perhaps in the final analysis results of the same thing. The corresponding parallelism between spreading and solubility in liquid-liquid-gas systems has already been specifically pointed out by Harkins[18] in taking up "insolubility as an accompaniment of non-spreading," along with the limitations which must be observed in applying the parallelism. Harkins also discusses the dependence of both phenomena on the value of the spreading coefficient, which is the difference between the adhesional work and the cohesional work for the liquid whose spreading or solution is being considered.

The authors also apply their solubility theory to the oiling of sulphide minerals that have been given a hydrocarbon surface by treatment with typical soluble collectors. If, following Professor Taggart and co-workers, we are to accept the idea that the surface is made up of definite chemical compounds formed by metathesis, and if we also accept the idea that the surface is soluble in the hydrocarbon oil, where do we arrive? We can avoid ambiguity only by qualifying the term "soluble" in the latter case; that is, by speaking of a solubility of only the hydrocarbon parts of the molecules on the mineral surface. This is not solution in the established sense of an intimate *molecular* mixture but a special kind of solution involving intimate mixing of a single plane of *atomic groups*, regardless of their molecular associations. Using the latter special concept of solution, the solution-oiling theory, applied to oiling of a surface after its reaction with a soluble collector, becomes an obvious statement qualitatively describing the nature of the surface region between the oil and the mineral surface. In contrast, the thermodynamic treatment in terms of the well-known surface-energy relations, contact angles and spreading coefficients, is quantitative and practically useful.

---

* Instructor, Department of Mining Engineering, Massachusetts Institute of Technology.

[18] See The Theory of Colloidal Behavior, edited by R. H. Bogue, **1,** 176. New York, 1924. McGraw-Hill Book Co.

In conclusion: a solution mechanism is one of molecular mixing; displacement of one fluid phase by another at the surface of a third phase is another manifestation of certain forces which also affect molecular mixing, but its mechanism involves molecular mixing only in a limited sense within the phase-boundary region. The solution mechanism may accompany the displacement mechanism, but it is entirely conceivable that the displacement phenomenon may occur alone, particularly if the tendency to mix exists only between parts of the moledules in one phase and is not strong enough for these parts to drag the whole molecules into solution.

O. C. Ralston,* College Park, Md. (written discussion).—The continued stream of interesting and excellent papers on various phases of mineral filming and separating processes that have emanated from the laboratories in the Columbia School of Mines for many years is a matter of gratification. They have had value from the standpoint of the academic, the practician and the litigant. May we have many more of them!

The authors' classification of nonsulphide, nonmetal minerals into four groups is useful, except that one might suggest a fifth class exemplified by the very soluble salt crystals that can be separated by flotation or agglomerate tabling methods in a saturated brine made up from these salts. They are not satisfactorily included in class 3. Since this is in commercial operation on the sylvite ores of New Mexico and a great variety of "salt mush" separations have been devised, it should be included.

The method of preparing and studying carefully polished surfaces of minerals as used at Columbia is elegant, but certain horrible doubts as to its validity are difficult to dissipate. The so-called "Beilby amorphous polish layer" formed on polished surfaces is not always of crystalline material but sometimes of the nature of a supercooled liquid or glass, as recently shown through the application of electron diffraction to various mineral surfaces by G. Ingle Finch.[19] Almost certainly the freshly polished surface of sulphur will be of amorphous material, not comparable to the crystalline rhombic sulphur cleavage surfaces commonly met in nature.

The senior authors of this paper have been advocates of a chemical filming theory of flotation which I have always regarded favorably but with the precaution not to pin all of one's faith to one mechanism when there is such a bewildering variety of minerals and reagents to consider. It is, therefore, pleasing to see now another or at least a modified theory further propounded; i.e., that minerals in the first group of the proposed classification are *activated only by oils in which they tend to be soluble*. However, once more I must object to generalizations that are too sweeping. With graphite and carbon the present authors have not worked with out-gassed specimens prepared in accordance with precautions developed by physical chemists working with pure forms of carbon. I shall refer to this in more detail later.

The present report on the filming and levitation of sulphur after suitable purification is of great value from the academic standpoint. However, the mineral sulphur as usually worked in nature is either the oil-contaminated brimstone of the sulphur domes in sedimentary rocks or the solfataric or volcanic sulphur resulting from action of hydrogen sulphide, sulphur dioxide, steam and air. No sample tested by the authors can include with certainty the behavior of volcanic sulphur. Taking the standpoint of a practical man interested in the concentration of the natural ores of sulphur, one learns little from this study except how the mineral would have behaved if it had been pure—which it never is—and if it had polished surfaces instead of cleavage surfaces. Therefore, one might ask if the authors have not been a bit severe in ascribing error to Sulman, Cattermole and co-workers, followed by Gaudin and by Wark and Cox (and, if justice is done, by the present writer) in ascribing inherent flotability to natural sulphur. We owe to the writers a better understanding of why brimstone from sulphur domes is such a natural or easy floater; it would be of value to learn whether the volcanic sulphur mineral behaves in the same way; we would appreciate some knowledge of the behavior of the sulphur recovered by gas purification processes; for instance, in the iron oxide "boxes" for removing water from manufactured gas.

---

* Chief Engineer, Nonmetals Division, U. S. Bureau of Mines.

[19] G. I. Finch: The Beilby Layer on Nonmetals. *Nature* (1936) **138**, 1010.

As a metallurgist with a physicochemical bias, I have watched (and participated slightly in) the development of flotation theory for over 25 years and have been disappointed in the physical chemistry of flotation as developed by nearly all of the metallurgical experimenters, but Wark and co-workers, in Melbourne, Australia, now under fire from the present authors, have in my judgment shown the soundest application of physical chemistry to the flotation problem.

The tests on graphite reported in this paper are not entirely convincing. There seems to be no cognizance taken of the tendency of carbon surfaces when heated in air to take up oxygen to form carbon-oxygen complexes that break down to release carbon dioxide and carbon monoxide at all temperatures but are not completely broken up even in vacuo at 1000° C. Starting with Rhead and Wheeler 20 years ago, a voluminous literature has grown up in which the more important recent names are N. A. Shilow, A. Frumkin, J. N. Mukherjee, M. M. Dubinin and Elroy J. Miller. The latter has a useful summary[20] discussing the basic and acidic reacting surface oxides of carbon. In the face of all this weight of evidence, the present authors' attempts to purify graphite by acid extraction followed by heating at "red heat" leave their samples in an indeterminate condition. Neglecting that aspect, and sympathizing with the desire to learn how some of these industrial minerals behave if obtainable in pure form, nevertheless the average reader of this paper has only an academic interest in a purified unnatural product and would prefer to know how natural minerals behave and how they can be concentrated usefully. From this angle, the paper leaves much to be desired.

A. B. Cox* AND I. W. WARK,* Melbourne, Australia (written discussion).—In defending their version of the chemical theory of the action of collectors, Messrs. Taggart, del Giudice, Sadler and Hassialis claim that, in so far as our criticism was based upon the reactions of sulphur and graphite, it is inadmissible. They concede, however, that arguments based upon the behavior of these two elements formed only part of the evidence cited by us against the theory. In our opinion, their present conclusions, even if they were acceptable in toto, would not support their theory. It is asserted that sulphur and graphite can be floated only after they have acquired a surface film of oil, and that only oils are collectors for these elements. We dissent from this view, though we agree that oils are collectors for both elements. Logically the authors should explain the acquisition of an oil film in terms of "chemical reactions of well recognized types."[21] This they do not even attempt, but rather rely on a nebulous explanation in terms of solubility. Thus they state that Nujol wets sulphur because sulphur dissolves in it. Presumably they must also assume solubility of graphite in mineral and other oils, an assumption that lacks experimental support. Subsequently it is stated that Nujol spreads to a unimolecular film on sulphur. We find it impossible to picture this process in terms of solubility: the term "solubility" can have its customary meaning only when phases in bulk are considered.

---

[20] E. J. Miller: *Jnl. Phys. Chem.* (1932) **36**, 2967–2980.

* Department of Chemistry, University of Melbourne.

We are not convinced that pure clean sulphur will not float without a collector. By adopting the methods described by the authors—namely, recrystallization from benzene followed by the nitrogen treatment—we have been able to confirm their results, but on continuing with what we regard as the only stringent test for air avidity, the result is different. Polished surfaces are usually covered by a thin film of abrasive or slimed mineral; on wiping the surface with a clean linen pad this is removed and the captive-bubble test then gives a truer indication of the condition of the surface and of how the mineral will behave in flotation. When polished sulphur was wiped in this way it invariably showed adherence with an air bubble. We interpret this as meaning that sulphur possesses air avidity, not that the surfaces were contaminated, but we realize that there is room for a difference of opinion. However, our interpretation is supported by the statement on page 186 that 80 per cent of the authors' purest sulphur floated in the absence of collectors.

Taggart and his collaborators are correct in stating that sublimed sulphur has an acid reaction, but we do not agree with them that the consumption of xanthate by sulphur is due entirely to this acidity. Even sulphur that has been twice recrystallized from benzene and shows no acid reaction does consume amyl xanthate and ethyl xanthate. An aqueous extract of the sulphur consumed no iodine; consequently the xanthate consumption (which was estimated by an iodine titration after filtration) was due to some reaction with, or to adsorption on the sulphur itself. The actual consumption by 3 grams of finely ground sulphur in 24 hr. was from 10 to 30 per cent of the xanthate in 10 c.c. of a 500 mg. per liter solution.

Flotation tests indicate a response to amyl xanthate. Roll sulphur, crushed very coarsely under water, hardly floats at all in a strong sodium chloride solution, though a fairly stable froth forms. Addition of 200 mg. per liter of amyl xanthate causes good flotation. This suggests that sulphur particles too large to float because of their own inherent floatability do float after becoming coated by amyl xanthate.

The authors are wrong in interpreting our statement that "amyl xanthate did not induce the customary angle of contact" as meaning that amyl xanthate failed to induce any angle of contact. What we implied was that the angle obtained was not the customary angle, but a little less. The angle of 60° obtained by the authors with 200 mg. per liter of ethyl dithiocarbamate suggests to us adsorption of the unchanged compound. The authors themselves suggest that the angle is due to an oily decomposition product of the carbamate, but remembering that the hydrolytic products corresponding to the concentration used are soluble in water, and that the first oxidation product, tetraethyl thiuram disulphide, is a solid, we cannot guess what oily decomposition product they had in mind. Likewise, it is difficult to reconcile angles of contact of 74° for sodium oleate and 60° for oleic acid with the suggestion that flotation by the former is due to the presence of the latter.

The estimation of potassium, mentioned on page 185,* is erroneous. From 1024 mg. per liter of potassium ethyl xanthate it is claimed that 27.2 mg. potassium per 50 c.c. was obtained, whereas the amount theoretically present is only 12.5 mg. per 50 c.c. In view of this, the summary of the second paragraph of page 191 is not as convincing as the authors desire. We do not suggest, however, that potassium ions are adsorbed by sulphur.

---

[21] Taggart, Taylor and Knoll: *Trans.* A.I.M.E. (1930) **87,** 217.

* See page 206.

Since the paper under discussion was written we have published a paper in which many of the points raised have already been discussed.[22] By using ash-free sugar charcoal, the presence of heavy metal impurities was avoided, and the possible formation of heavy metal xanthates was prevented. Nevertheless, xanthates were adsorbed by this charcoal. With graphite, an amount of alkali (including carbonate) was liberated equivalent to the xanthate removed. The reaction is:

$$\underset{\text{(adsorbed)}}{\text{OH}} + \underset{\text{(dissolved)}}{\text{EtX}^-} = \underset{\text{(adsorbed)}}{\text{EtX}} + \underset{\text{(dissolved)}}{\text{OH}^-} \qquad [1]$$

The adsorbed hydroxyl arises from an initial adsorption of oxygen and water. With sugar charcoal a second reaction is possible, namely:

$$\underset{\text{(adsorbed)}}{\text{H}} + \underset{\text{(dissolved)}}{\text{K}^+} = \underset{\text{(adsorbed)}}{\text{K}} + \underset{\text{(dissolved)}}{\text{H}^+} \qquad [2]$$

and the amount of alkali liberated by the total adsorption corresponds to the difference between the xanthate and potassium ions adsorbed. Even when potassium and xanthate ions are both adsorbed, it is incorrect to say that potassium xanthate is adsorbed, as a consideration of the above mechanism will show. In our first paper we stated explicitly, on both theoretical and experimental grounds, that the xanthate ion (and not potassium xanthate) is adsorbed by graphite. Apparently this was missed by our critics, for on page 191 is the statement that, according to us, graphite is coated by alkali (metal) ethyl xanthate, and therefore that washing with warm water should remove the xanthate. The fact that washing did not remove xanthate is regarded as opposing our views, whereas we thought that we had made it clear that our views are consistent with the result: they were, in fact, based partly upon this result.

On page 187, the authors actually recorded an increase in alkalinity upon treatment of graphite by xanthate. This is in accord with equation 1 above, but the authors suggest that it results from a decomposition of the xanthate of such a nature that oily products of the sulphide type are formed. In making this deduction the authors ignore our experiment of 1935, in which it was shown that the xanthate removed by graphite is not in an oxidized condition, for it can be estimated by means of an iodine titration.

We are surprised at the results obtained with the National Carbon graphite, particularly with amyl xanthate, and suggest that the ineffectiveness of the xanthate may have been due to the low concentration (5 mg. per liter). We do not know the history of this graphite, but we do know that the previous history of sugar charcoal has an influence upon its adsorptive properties. We have recently prepared sugar charcoal free from contamination by heating it to a red heat and quenching in water. With this charcoal, which showed no tendency to float in 50 mg. per liter terpineol solution, addition of 200 mg. per liter of freshly purified amyl xanthate caused excellent flotation. With this comparatively high concentration of collector it might be suggested that sufficient oxidation to disulphide could occur to give an oil film. Consequently we substituted secondary octyl xanthate for the amyl compound, and found that 10 mg. per liter in conjunction with terpineol as frother gave excellent flotation.*

---

[22] I. W. Wark and A. B. Cox: Adsorption of Xanthates by Activated Carbon and Graphite and Its Relation to the Theory of Flotation. *Jnl. Phys. Chem.* (1937) **41**, 673.

* It is advisable to add the frother last, otherwise the xanthate tends to destroy the froth. Flotation is not permanent: a fresh addition of xanthate is necessary after

Other soluble organic compounds, from which oils are not readily derived, are effective collectors for sugar charcoal. Thus 250 mg. per liter of hexylamine hydrochloride or 100 mg. per liter of n-butyl ammonium iodide are excellent collectors, no additional frother being necessary with the former. On the other hand, aniline hydrochloride is not a collector for sugar charcoal though at 2.5 grams per liter it is good frother. It is concluded that adsorption of soluble organic compounds by carbon is not universal, and that adsorption by carbon is not confined to oils. It may be objected that we are not dealing with a pure carbon surface, for quenching would tend to produce adsorbed hydrogen and carbon monoxide. (It should be noted that such a surface would be highly reducing and not likely to result in oxidation of xanthates.) In so far as we are concerned with the chemical theory of collection, this objection is immaterial, for the theory fails if instances can be cited in which a solid adsorbs an air-avid film from solution without forming a definite chemical compound. Several such instances have been cited.

In accepting the challenge of Professor Taggart and his colleagues, we have the hope that a full discussion of the points at issue will lead to a better understanding of the principles of flotation, which, apart from its contribution to pure science, cannot fail to benefit the practice of ore dressing.

A. M. GAUDIN,* Butte, Mont.—I am inclined to believe that several mechanisms are operating in causing collection. If we like to call them all chemical reaction and make the definition of chemical reaction wide enough to include that, I am in accord.

Specifically, in this paper I find an extremely interesting experimental inquiry, into the behavior of sulphur particularly. I have, however, wondered if the authors have not displaced one kind of contamination by a more pleasant kind, by a kind of contamination that would not stick to air. Sulphur, we know, reacts with oxygen very readily. I see no reason why sulphur should not be contaminated with sulphur dioxide if it is not contaminated by carbon disulphide or if it is not contaminated by the petroleum oils. In other words, I am not sure that the authors have established that the sulphur is pure. Of course, if the sulphur that they have prepared and worked over and labored over is not pure, the whole argument that sulphur is not floatable per se has no value. I think that is one point that should be made beyond equivocation.

Another point that interested me was the admission that collection of the sulphur could occur by dissolution of the surface in a volatile compound like benzene, a volatile compound that then could not be driven off even though heated to a temperature very considerably above its boiling point. That I think is prima facie evidence of adsorption, so if this flotation of sulphur by adhering benzene is a fact, I think evidence has been presented by the authors of flotation by adsorption rather than by chemical reaction.

The philosophy of the paper amounts to this: That about the only things that will stick to air or gasses in general are hydrocarbons and carbon disulphide. Perhaps that is so, but I see no reason why other things should not also belong there—why sulphur and carbon and some sulphides should not belong there also. That is a difference of viewpoint that some of us hold among ourselves.

The authors should be congratulated in presenting evidence that is such a decided contribution to our understanding of the fundamentals of flotation.

---

a few minutes. Presumably as xanthate becomes adsorbed in the pore spaces its availability is lowered. A similar condition arose when using cetyl trimethyl ammonium bromide.

* Research Professor of Mineral Dressing, Montana State School of Mines.

M. Hassialis.—I was rather surprised to hear about the two contaminants, sulphur dioxide and benzene. That is not in accord with experimental facts because if there had been any sulphur dioxide present, a water extract should have shown sulphurous or sulphuric acid as indicated by the pH of that solution, and yet we found in more than one case that the extract was near chemical neutrality.

A. M. Gaudin.—That is true providing sulphur dioxide does not stick to the sulphur, as it might be sticking. You might get the acid reaction only if there were an excess of sulphur dioxide that could be dispensed with.

M. Hassialis.—Is not that the same thing as the statement that there is no partition of sulphur dioxide between the water and the sulphur, and you know that it is one of the fundamental principles that materials will partition between two phases?

A. M. Gaudin.—The partition may be so far over one way as to make it inappreciable by the technique that you have adopted.

M. Hassialis.—But the test for chemical neutrality is very sensitive.

A. M. Gaudin.—It may not be sensitive enough.

M. Hassialis.—There is one further consideration: If there were sulphur dioxide present, that should, after 16 hr. contact, at least decompose some of the xanthate to the point of the decomposition products. In an attempt to progressively remove the benzene, we found that in our first attempt we could readily displace the water from the surface of the sulphur product by air, and yet on further treatment of the same sulphur, specifically I refer to the attempt with the nitrogen, we obtained a sulphur product which eventually did not have water displaced from its surface by air. That is not proof that the benzene was completely removed, but it certainly is indicative.

A. M. Gaudin.—It seems to me you stated that you heated the sulphur in air.

M. Hassialis.—First in air.

A. M. Gaudin.—And you passed nitrogen through it.

M. Hassialis.—Then reduced pressure with nitrogen going through it.

A. M. Gaudin.—Of course, the nitrogen might have had a very small quantity of oxygen, and, dealing with the kind of things that you have been dealing with, it seems to me that you are entitled to a suspicion that perhaps the oxygen had a part in oxidizing the sulphur.

In some experiments we made some years ago on grinding and in floating in the absence of oxygen we were sadly disappointed because we could not get nitrogen that was free enough of oxygen for our purpose, even after passage through glowing copper and through a solution of pyrogallol. We still had 0.01 per cent, or some such amount, of oxygen, which was doing much more damage than its weight would indicate.

M. Hassialis.—I do not say that we can never completely remove the oxygen from anything. That would be a ridiculous statement; that is, I doubt that the last trace can ever be removed, but the point is that the results of the experiments cited by Wark and Cox as to the properties of sulphur should not be ascribed to the sulphur but to contaminants contained therein, and as such if we can reduce the contaminants to a concentration that is too small to materially affect the reactions that they cite I think that is again indicative of our point.

A. M. Gaudin.—It seems to me that there are several points in your paper, and I was not siding with Messrs. Wark and Cox. I was taking issue with another point in your paper—to wit, that the sulphur that you were securing by your coddling was pure sulphur on the outside. I am not satisfied that it was, and I do not know that anyone can make pure sulphur, and I raise the question that perhaps you have replaced one kind of impurity by another kind of impurity.

M. Hassialis.—One that is not affecting these results.

A. M. Gaudin.—It might be effective in the sense of making the sulphur nonadherent to air, whereas the other kind of impurity which you remove is effective in making it adherent to air.

P. S. Roller,* College Park, Md. (written discussion).—It appears to me that a unification, though by no means identification, of the chemical and adsorption theories of flotation, results when the subject is treated from a thermodynamic viewpoint. In flotation we have to consider the interaction between a mineral surface and a collector, activator, or depressor in which a stable molecular film is formed at the surface. Thermodynamic theory states that a stable film will be formed if free energy is liberated in the reaction. The greater the decrease in free energy, the more stable will be the film.

In thinking of a possible flotation reaction, we must, by thermodynamic necessity, ask ourselves whether the action is accompanied by a decrease in free energy. For the purpose of estimating the order of magnitude of the energy change, we may divide possible reactions into three types: The first type includes reactions in which an ionic or a covalent atom bond is formed. The free energy decrease is very high. To this class belong those chemical reactions in which atom bonds are formed, such as the chemical reaction of double decomposition. When a flotation reagent reacts in this sense with a mineral surface, a very stable molecular film will result because of the large decrease in free energy. The second type of reaction is that due to dipole interaction or to the formation of coordinated covalent bonds. The free energy decrease is moderate. Many reactions of simple solution fall in this class. A reaction of the second type may be expected when two molecules of high dipole moment, or molecules containing an even but incomplete number of outer shell electrons come into contact. The third type of reaction is that due to the attraction of higher dipoles, sometimes called dispersize or Van der Walls attraction. The free energy decrease is very small. To this type belong those reactions in which the molecules have a nonpolar rare gas configuration.

Because of the relatively large decrease of free energy that accompanies it, we are forced to consider, primarily, a reaction of the first type, or a chemical reaction between mineral surface and collector, as the mechanism by which flotation takes place. Failing this, a reaction of the second type of lower energy liberation may be entertained. We are thus led by thermodynamic considerations to the same viewpoint that Prof. A. F. Taggart and his school have advanced with so much originality and painstaking experiment.

Being unable to conceive first an atomic, or secondly a molecular reaction, one might feel constrained to consider the third type of reaction as a mechanism of flotation. However, the energy effect here is so small that the possibility of a sufficiently stable molecular film can be discounted.

Rather than entertain the possibility of a low energy film, it would be much more fruitful to consider impurities as a cause of possible high-energy atomic or molecular reaction. Impurities at a mineral surface may arise in different ways. They may exist in the mineral itself, or originate in the gangue, in the flotation reagent, or in other sources, or they may be formed by the action of air or other gas on the mineral surface. The importance of impurities as a cause of stable films has been amply stressed and exemplified by Taggart and co-workers.

---

* U. S. Bureau of Mines.

A few words may be said about the relation between surface tension and free energy. By thermodynamics, surface tension is simply free energy per unit surface. Hence, the statement that a film is formed at a surface due to lowering of the surface tension is wholly equivalent to the statement that it is due to a decrease in free energy.

Adsorption of a solute at a surface by Gibbs' equation is not any mysterious exception to the principle of free energy change as a determinant of film formation. Gibbs' equation is simply a secondary thermodynamic relation between surface attraction and osmotic pressure. It tells us what is the excess of solute that may be held by surface forces against the osmotic pressure of the excess solute. The amount that is held need not be greater than a monomolecular film. If an excess beyond a monomolecular film produces no further change in free energy (surface tension), no film greater than monomolecular will form.

Gibbs' equation tells us nothing about the nature or cause of the adsorption itself. The adsorption however is nothing more nor less than the product that arises from a reaction that results in a decrease in free energy. The reaction can in fact be described in terms of the types listed above. A reaction of some intensity is in fact presupposed and is a prerequisite to any application of Gibbs' equation.

A. M. Gaudin.—I have a message from Mr. James Wilding, who expressed his regret on not being able to be here this afternoon. Mr. Wilding asked me to submit a fact which he thinks will be of interest in connection with this general discussion. I read from his letter as follows:

"*Florida Phosphate Ore Treated with Calcium Lauryl Phosphate and Fuel Oil and Floated by Froth Flotation*

| | Weight, Per Cent | B.P.L., Per Cent | Distribution, Per Cent |
|---|---|---|---|
| Heads | 100.0 | 25.92 | 100.0 |
| Concentrate | 31.3 | 67.00 | 80.8 |
| Mids | 10.3 | 21.50 | 8.6 |
| Tails | 58.4 | 4.70 | 10.6 |

"Agents: Calcium lauryl phosphate, 1.5 lb. per ton of ore; fuel oil, 9.4 lb. per ton of ore. Rougher concentrate retreated without additional agents."

The interesting thing is that in calcium lauryl phosphate there is nothing to react with the mineral that is floated and that it is substantially water-insoluble.

A. F. Taggart (written discussion).—Generally as to Professor Gaudin's comments that we might have done this or we might have done that, we take the position that we did the things related in our paper; that the extent of purity of the resultant sulphur and carbon that we used was that indicated by the tests cited in the paper and the oral discussion, and that when such a degree of purity was achieved—whether it was absolute or not is beyond the question—collection by xanthates did not take place, and the so-called natural floatability of sulphur and of graphite did not manifest itself.

Mr. Ralston reproves us for not telling him—if he is an average reader—"how natural minerals behave and how they can be concentrated usefully." We refer him to an already voluminous literature. We are concerned here with "whys." We do not believe that the possibility of a Beilby layer on our polished sulphur surfaces affects in any way our conclusion that sulphur coating by oils is due to solubility of the sulphur in the oil. We would even be willing to dress that relatively simple explanation up a bit, lug in the second law of thermodynamics, and say that the spreading occurs because of the relatively low interfacial energy of the oil-sulphur interface, which flows, of course, from this self-same solubility. Neither do we feel that the well-known, although not well-defined, oxygen-carbon equilibria, to which Mr. Ralston refers, have anything to do with the case in point. The fact is that the oxidation of carbon, whatever its extent, was insufficient to prevent coating of the purified graphite with tar oils. Further, we see no reason to appeal to it for explanation of the fall in xanthate activation of commercial graphites with acid extraction and calcining. That phenomenon varied concomitantly with removal of iron; and iron, as we have established here at Columbia, will react with xanthate ion to form an activating coating.

Mr. Wilding's contribution as to the use of calcium lauryl phosphate as an activator in phosphate flotation seems to us to be possibly another manifestation of the phenomenon involved in the flotation of, say, galena with lead xanthate (see U.S. Patent No. 1512139, R. E. Sayre). This we have verified qualitatively at Columbia, with, however, no great assurance that xanthate ion was not introduced as an impurity in some form other than in association with lead. If we assume that our lead xanthate was pure, its activity in floating galena is explicable on the ground that a monomolecular layer of lead xanthate on a galena surface is less soluble than bulk lead xanthate.[23] Similarly, calcium lauryl phosphate might be expected to exchange from the bulk form to a monomolecular surface coating on tricalcium phosphate particles in a phosphate pulp. This is the more to be expected since the phosphate-concentrate pulp treated was probably somewhat alkaline.

We are thankful to Messrs. Wark and Cox for pointing out the error on page 6 of the original paper. Potassium was calculated as potassium sulphate, 27.2 mg., and should have been so reported. Correction has been made in this volume (p. 185). With respect to the results of the further experiments with sulphur and carbon reported in their discussion, we have not further experimented to know whether we could verify them or not. We do know, however, that sugar charcoal and activated carbon are no more to be considered pure carbon than commercial sulphur and graphite are to be considered pure sulphur and graphite, respectively. We are inclined, therefore, at the moment to accept their statements of experimental data at their face value, with the sole reservation that neither they nor we know just what it was that they treated with flotation reagents, and to continue in our stand that graphite and sulphur do not constitute exceptions to the rule enunciated in the paper by Taggart, Taylor and Knoll (incompletely quoted in the first paragraph of the current discussion by Messrs. Cox and Wark), viz:

"All dissolved reagents which, in flotation pulps, either by action on the to-be-floated or on the not-to-be-floated particles affect their floatability, function by reason of chemical reactions of well recognized types between the reagent and the particle affected."

---

[23] See Taylor and Knoll: *Trans.* A.I.M.E. (1934) **112**, 392.

# A Cyanide Process Based on the Simultaneous Dissolution and Adsorption of Gold

By T. G. Chapman,* Member A.I.M.E.

(New York Meeting, February, 1939)

The writer has carried on experimental work for several years with respect to the simultaneous dissolution of gold by cyanide and the adsorption of the dissolved gold on activated charcoal in ore pulps, followed by the recovery of the charcoal by flotation.

The results of this experimental work have been sufficiently encouraging to suggest a new process based on the principle of simultaneous dissolution and adsorption of gold, applicable to certain ores and tailings that cannot be treated to advantage by countercurrent decantation or filtration. Applications for patents have been filed and The Dorr Company, Inc. has the exclusive right to license the use of the process.

The purpose of this paper is to describe such a process, state its possible advantages and immediate field, and give some results obtained on a laboratory scale.

## Early Experimental Work

In the early stages of the experimental work attempts were made to precipitate soluble gold from cyanide solutions with zinc and aluminum in ore pulps followed by flotation of the precipitated gold, but since the results were not promising enough to continue with these precipitants attention was directed to carbon. The first experiments with carbon comprised the addition of cyanide and alkali to the ore pulp, the addition of carbon at or near the end of the dissolving period, and the recovery of the carbon by flotation. With this method of procedure the assumption was made that carbon functioned as a precipitant of gold from cyanide solutions and as such should be added as are other precipitants, including zinc and aluminum; namely, at the end of the dissolution period. The assumption was then made that carbon functioned as an adsorbent, and that if such assumption proved to be correct, it could be added with success to the ore pulp at the time of adding the cyanide. The first experiment along this line was successful in that the feasibility of the dissolution of gold by cyanide and the simultaneous extraction of the dissolved gold by carbon in ore pulps was demonstrated, at least with respect to such treatment on a laboratory scale.

---

Manuscript received at the office of the Institute Jan. 16, 1939. Issued as T.P. 1070 in Mining Technology, May, 1939.

* Professor of Metallurgy, University of Arizona, Tucson, Arizona.

## ACKNOWLEDGMENTS

The writer was assisted in the experimental work by Prof. A. J. Thompson and advanced students in metallurgy at the University of Arizona, including F. L. Evans, N. D. Houghton, Jr., L. R. Mayne, G. E. Meaders, R. C. Meaders, S. M. DePoy, D. D. Rabb, C. H. Sandberg, and J. H. Soule, and he gratefully acknowledges the aid of these men. The writer is especially indebted to S. M. DePoy for the discovery of a new reagent for the flotation of activated carbon, and to Dean G. M. Butler, of the University of Arizona, and Prof. C. E. Locke, of the Massachusetts Institute of Technology, for kind encouragement during the course of the experimental work.

## FLOWSHEETS

Figs. 1 and 2 give two suggested flowsheets for the treatment of tailings and ores, respectively, by the proposed simultaneous dissolution and adsorption process. The essential difference in the flowsheets is that the first employs a single addition of activated carbon and the second uses two additions of carbon, with the first separated from the ore pulp by flotation before the second is added. The assumption used in both flowsheets is that grinding is required. For the treatment of tailings that do not require grinding, or for the treatment of slimes separated from ground ores, the grinding circuits would be omitted.

## PROPOSED FIELD OF PROCESS

Although some experimental evidence is available that indicates possible advantages of the proposed process in treating certain ores as compared to countercurrent decantation or filtration methods with respect to recovery, rate of dissolution of gold, low strength of cyanide permissible, and capital cost of plant, other considerations may outweigh at present the possible advantages that have been mentioned. It is not suggested, therefore, that the process in its present state of development can compete with current cyanide methods when the ore to be treated is readily amenable to these methods.

As previously stated, the writer does believe, however, that the simultaneous dissolution and adsorption process offers considerable promise of successfully treating tailings and ores that cannot be treated to advantage by current cyanide methods, and the discussion and experimental data presented in this paper are directed particularly to the treatment of such ores and tailings.

## RECORD OF CARBON IN CYANIDATION IN THE LITERATURE

A bibliography covering experimental work and the use of carbon in cyanidation up to about 1926 was given by Gross and Scott[1] and later applications of carbon to cyanidation have been recorded by Dorr.[2] Since the record of the use of carbon in cyanidation is rather voluminous, and has been so recently and completely recorded by the authors men-

---

[1] References are at the end of the paper.

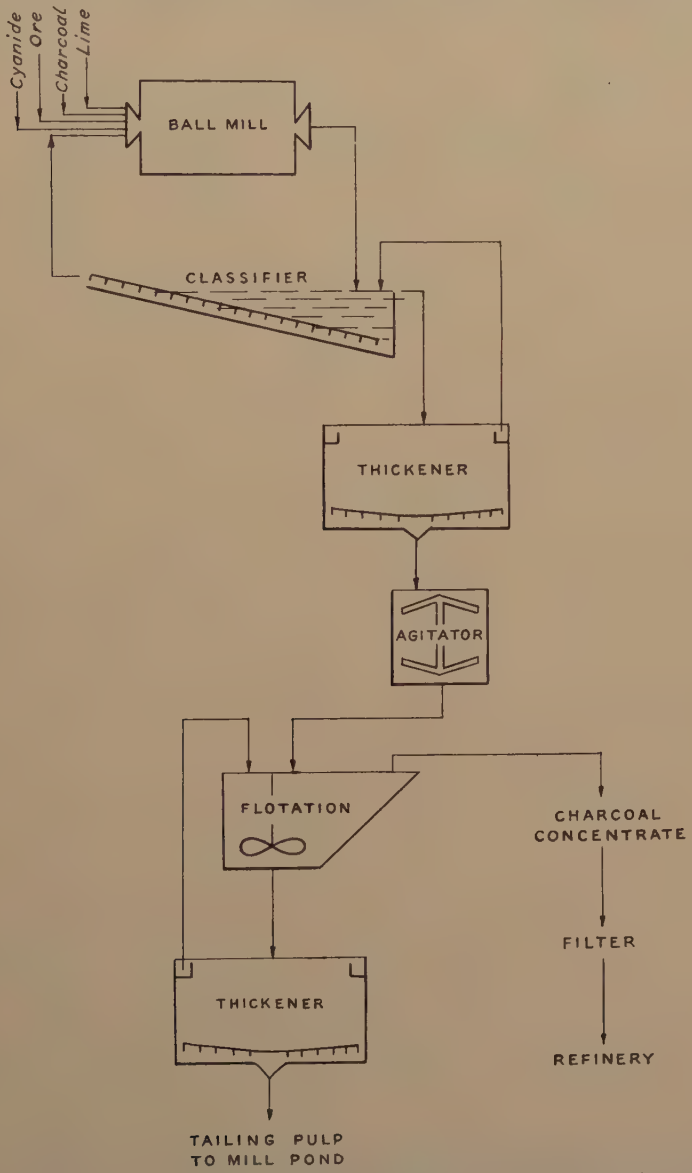


Fig. 1.—Flowsheet of single-stage simultaneous dissolution and adsorption cyanide process.

tioned, the writer will not refer further to previous work except to acknowledge specific work of special interest with reference to the process described.

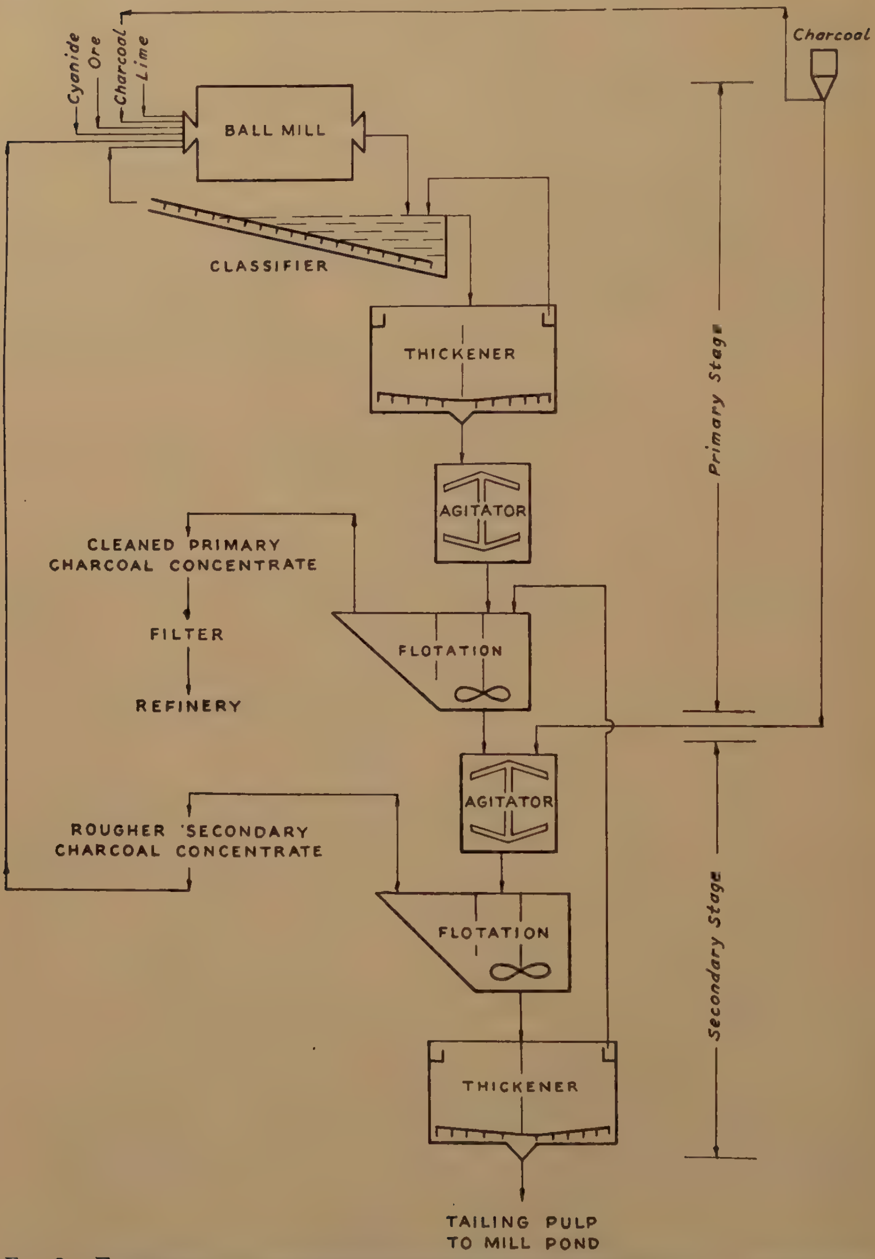


FIG. 2.—FLOWSHEET OF DOUBLE-STAGE SIMULTANEOUS DISSOLUTION AND ADSORPTION CYANIDE PROCESS.

## Simultaneous Dissolution and Adsorption of Gold

In a process employing dissolution of gold with simultaneous absorption of the dissolved gold, the concentration of gold in the solution during the course of the dissolution and adsorption will depend upon the relative rates of dissolution and adsorption. The rate of dissolution of gold from ores by cyanide depends primarily upon such variables as fineness of the gold particles, accessibility of the particles to the solution, and the degree of agitation employed in bringing into rapidly changing contact the gold particles, free cyanide, and oxygen. It is obvious that the average rate of dissolution of the gold will vary with each ore and the only similarity that the writer has noted with respect to dissolution rates of various gold ores is that the rate of dissolution with most ores is very rapid at the beginning of contact with the cyanide and progressively decreases as the dissolution period advances. Referring now to the rate of adsorption of the dissolved gold in ore pulps by activated carbon, it is a matter of experimental record that the rate is rapid as compared to the usual dissolution rates providing sufficient properly activated carbon is present in the ore pulp. It follows, since the rate of adsorption can keep pace with the rate of dissolution, that a solution of low gold content will be maintained throughout the dissolving operation, providing sufficient properly activated carbon is added with the cyanide as contrasted to a solution varying from a minimum gold content at the beginning to a maximum gold content at the end of dissolution with current cyanide methods.

Among the possible merits of simultaneous dissolution and adsorption, which results in maintaining a low concentration of gold in the solution, the following are given:

1. The possibility of soluble gold being adsorbed at the surfaces of ore constituents is reduced to a minimum.
2. By the law of mass action, since the gold is removed from the solution as rapidly as dissolved, the avidity of the solution for gold is maintained at a maximum, thus insuring the maximum speed of dissolution of the gold.
3. The separation of the dissolved gold from the ore pulp is not dependent upon the settling rates of finely divided solids, the amount of dilution available as in countercurrent decantation methods, the uniformity of a filter cake, or the mechanical displacement of pregnant solution by washing as in filtering.
4. In addition to the foregoing there is the advantage of simplicity in the combining of two operations—namely, dissolution and adsorption—in that a separate mill unit is not required for each.

Referring to the first advantage given—decreasing the adsorption of soluble gold upon the surfaces of ore constituents—the writer does not believe that appreciable losses due to such adsorption occur with gold ores comparatively free of certain finely divided constituents usually referred to as colloids. Considerable evidence is available, however, indicating that losses of soluble gold occur in washing operations during the treatment of ores that contain appreciable amounts of certain so-called colloids. While the cause or causes of such losses may be disputable and vary with respect to the treatment of each ore, it appears reasonable that such losses may be explained in part by the imperfections of the mechanical operations of countercurrent decantation and filtration, in part by adsorption of soluble gold upon the surfaces of colloids, and in part by the entangling of pregnant solution due to flocculation by lime.

Julian and Smart[3] made the following statement in 1921 or earlier with respect to the possibility of adsorption affecting results in the cyanidation of ores:

> The adsorptive power of charcoal has a distinct bearing on the cyanidation of ores, and this substance causes a loss of metal when it is inadverently included with the ore for treatment. . . . . . . . . . .
>
> Investigations have shown that other substances besides charcoal have marked adsorptive properties. Among these may be mentioned clay and kaolin. Colloidal substances would seem to possess absorptive as well as adsorptive properties. Adsorption phenomena are developed to a considerable degree in the cyanide process, where there is an enormous area of contact-surfaces between the solids and the solution, and with media, such as silica or hydroxide of iron, highly favorable for producing the effects.

Although Julian and Smart did not present specific data to show that soluble gold is adsorbed by colloids, they did present the results of Gore's experiments with reference to the adsorption of sodium cyanide by finely divided precipitated silica, and these results indicated a very appreciable adsorption of sodium cyanide and are in line with present-day accepted experimental evidence to the effect that as the concentration of the sodium cyanide in the solution increased the amount of sodium cyanide adsorbed per unit of the adsorbent used increased.

That Hamilton[4] recognized the possibilities of adsorption of soluble gold on the surfaces of colloids is indicated by his statement in connection with his description of countercurrent decantation methods:

> Another phenomenon, rather difficult to explain, is also sometimes in evidence in the use of this process. Even in cases where little or no dissolving action is observed in the successive thickeners in which cyanide solution is used as the diluent yet when the pulp reaches the last thickener and is diluted with water marked dissolution of the metals seems to take place. This may perhaps be due to the increased activity of the ions in a less viscous medium than is afforded by the stock solution. On the other hand, it seems possible that the dissolving effect may be only apparent and that in reality the result may be due to a liberation of pregnant solution previously adsorbed by the colloidal constituents of the pulp. Such a liberation might conceivably be

brought about by the changes in the properties of the electrolyte due to excessive dilution with water. One such change might be traced to a decrease of lime in solution sufficient to cause the curds or aggregations of clayey matter to disintegrate into their original units liberating soluble matter which had been entangled with them.

The writer suggests another explanation for possible apparent dissolution of gold in the last thickener of a countercurrent washing system; namely, that with stock solutions used in washing operations the adsorbed gold if present on the surfaces of the colloids is in equilibrium or nearly in equilibrium with the concentration of gold in the solution, but when fresh water is added to the pulp in the last thickener the equilibrium is disturbed, causing part of the soluble gold on the surfaces of the colloids to migrate to the solution. The reversibility of adsorption reactions between gold in the solution and adsorbed gold on charcoal has been demonstrated by others and confirmed by the writer, and if soluble gold adsorbed on charcoal migrates to the solution when equilibrium is disturbed, is it not possible that soluble gold adsorbed on colloids will migrate to the solution when the equilibrium is disturbed by the addition of a large volume of fresh water?

Summarizing, if some finely ground gold ores contain colloidal constituents capable of adsorbing soluble gold, the amount of gold adsorbed will be a function of the concentration of gold in the pregnant solution. Any depletion of gold concentration in the solution will result in a decrease in the amount of gold adsorbed by colloids and the minimum adsorption by colloids will occur when the solution is maintained at a minimum concentration of gold at all times, a condition that results when sufficient properly activated carbon is added at the beginning of the dissolution period.

Experimental evidence with respect to tests made by the writer with La Colorada tailings indicates that the original cyanide treatment of this material resulted in appreciable losses of soluble gold, especially in the treatment of the slimes. This tailing, amounting to between 1,500,000 and 2,000,000 tons, from amalgamation and cyanide treatments many years ago, is in Sonora, Mexico. The sands and slimes, about equal in amount, were stacked separately, the sands no doubt resulting from percolation treatment and the slimes from agitation and filtration. In testing the slime portion of this tailing, recoveries ranging from 65 to 88 per cent of the gold were obtained by the simultaneous dissolution and adsorption process without grinding. The tailing does not contain sulphides and therefore the recoveries mentioned cannot, the writer believes, be attributed to oxidation and decomposition even although the material has been exposed to such agencies for many years. The solubility of the gold in cyanide of the sand portion without grinding is approximately 10 to 15 per cent, indicating a much lower soluble gold loss in comparison with the slime portion, as would be expected. Although part of the soluble gold loss in this material was no doubt due to less efficient equipment in use many years ago as compared to modern equipment, experimental evidence indicates that, even with the equipment available today, the recovery by countercurrent decantation methods is approximately 60 per cent as compared to an average of 76 per cent for the simultaneous dissolution and adsorption process. The writer suggests the possibility that part of the gold contained in this tailing was due to adsorption and that the ability of the simultaneous dissolution and adsorption process to recover the major portion of the gold in this material without further grinding indicates a method for reducing adsorption losses to a minimum if such losses occur.

## Possible Applications of Process

Considering the four possible advantages previously suggested in favor of the simultaneous dissolution and adsorption process, it would appear that the immediate field of application would be in the treatment of difficult ores of the classifications that follow.

1. Ores and tailings containing large amounts of finely divided constituents of such character that the settling rate of the solids is too slow for practical countercurrent decantation operations. Ores of this class also present difficulties to filtering, which ordinarily would render this method of separating the pregnant solution from the solids impractical. Ores of this class would suffer most in recovery by possible adsorption losses when treated by current cyanide methods. Since such ores and tailings cannot be economically treated by current methods, and as experimental data given in Tables 1 to 4, inclusive, indicate that these ores and tailings can be treated by the process described, it is believed that this field is the most promising one immediately available.

2. The difficulty of treating gold ores containing graphite is well known and such ores offer a possible field in that the loss of soluble gold in them is probably due to adsorption. In the simultaneous dissolution and adsorption process the graphite, if present in the ore, functions as charcoal of a relatively low adsorption power and consequently works with the charcoal, as contrasted to opposition when such ores are treated by countercurrent decantation or filtration methods.

3. Certain mixed ores with part of the gold intimately associated with sulphides and consequently insoluble in cyanide offer a potential field. Some encouraging indications have been obtained in the treatment of a few such ores in that part of the refractory gold has been floated with the charcoal. No further general statement can be made with respect to ores of this class because results vary in the treatment of different ores.

4. The simplicity of the single-stage flowsheet would appear to offer an advantage in the treatment of low-grade ores and tailings.

## Single-stage and Double-stage Flowsheets

The simultaneous dissolution and adsorption process as indicated in Figs. 1 and 2 may be used in practice with one or two successive additions of carbon known as the single-stage and double-stage processes, respectively. The double-stage process yields a higher recovery than the single-stage, and should be used for ores. The single-stage process, because of the simplicity of flowsheet, is in general adapted to the treatment of low-grade tailings.

The disadvantage of the single-stage flowsheet for the treatment of material other than low-grade tailings is the large amount of charcoal found to be necessary to obtain acceptable barren solutions and the probability of incurring a loss of high-grade gold-bearing charcoal in the flotation operation. It is possible, of course, that future developments of the process including the preparation of more efficient charcoal for the adsorption of gold, and more experience in the flotation of charcoal, will eliminate the necessity of the second stage, but at present the single-stage process is at a disadvantage when maximum recovery and the use of minimum amounts of charcoal appear more desirable than a simplified flowsheet.

The two-stage process was suggested by the results of experimental work, which showed that: (1) the amount of gold adsorbed from a cyanide solution is greater if two separate, properly proportioned additions of charcoal be used in series, with the removal of the first before the second is added, than if all the charcoal is added as one lot, the total amount of charcoal used for the double-stage and single-stage adsorptions being the same, and (2) losses of gold-bearing charcoal, incurred in a primary flotation operation, can be essentially completely recovered under normal conditions by adding fresh charcoal to the tailing pulp and refloating.

The fresh charcoal added to the secondary stage in some cases constitutes all the fresh charcoal added in the process, since this charcoal after it is recovered by flotation is in the treatment of some ores advanced to the primary circuit.

## Recovery of Soluble Gold by Two-stage Adsorption

The experimental results indicating the advantages of two-stage adsorption were first secured in the adsorption of gold from clear solutions, and these results were later confirmed in the adsorption of soluble gold from ore pulps. Table 1 gives the results of single and double adsorption from clear solutions of varying gold contents using equal amounts of activated charcoal. Results of single and double adsorptions of soluble gold from ore pulps may be obtained by comparing the total gold contents of the primary and secondary barren solutions of Table 2, sections *D* and *E*.

TABLE 1.—*Comparison of Single-stage and Double-stage Adsorptions from Clear Solutions*

| | One Stage | Two Stages | One Stage | Two Stages | One Stage | Two Stages | One Stage | Two Stages |
|---|---|---|---|---|---|---|---|---|
| Assay of solution, oz. gold per ton | 0.04 | 0.04 | 0.14 | 0.14 | 0.40 | 0.40 | 0.40 | 0.40 |
| Total charcoal used, lb. per ton of solution | 4 | 4[a] | 6.6 | 6.6 | 6.5 | 6.5 | 13.0 | 13.0 |
| Gold adsorbed in primary agitation, per cent | 97.1 | 94.0 | 95.1 | 92.3 | 94.3 | 82.9 | 98.9 | 94.4 |
| Gold adsorbed in secondary agitation, per cent | | 5.0 | | 6.3 | | 15.5 | | 5.4 |
| Total gold adsorbed, per cent | 97.1 | 99.0 | 95.1 | 98.6 | 94.3 | 98.4 | 98.9 | 99.8 |

[a] Added in two successive lots of 2 lb. each per ton of solution.

## RECOVERY OF CHARCOAL IN SECONDARY FLOTATION

Referring to the recovery of charcoal by flotation, it would appear that the practically complete recovery of carbon would be a requirement for any charcoal process used for the treatment of material other than low-grade tailings. Since flotation is a mechanical process, it is expecting considerable to hope that a complete recovery of charcoal can be effected in a single-stage operation, especially under varying mill conditions. Experimental work has indicated that even under uniform flotation conditions some charcoal escapes recovery in the primary flotation operation and, further, that this loss may be recovered by the addition of fresh charcoal and refloating.

In Table 2, the gold contained in the secondary charcoal product represents the combined recoveries of additional gold adsorbed from the primary barren solution and gold contained in charcoal which escaped recovery in the primary flotation operation. The additional gold recovered in the secondary circuits as given in Table 2 varies from 3.3 per cent in Table 2*D* to 21.9 per cent in Table 2*A*.

## ADVANCING CHARCOAL FROM SECONDARY TO PRIMARY STAGE

Referring to Fig. 2, part of the new charcoal used is added to the grinding circuit and part to the agitator of the secondary stage. The charcoal added to the secondary agitator is recovered as a rough flotation concentrate and advanced to the primary circuit. With this method of operation the primary circuit operates for a high-grade charcoal concentrate and the secondary circuit for maximum recovery both with respect to further adsorption of gold from the solution and the recovery of possible losses of charcoal incurred in the primary flotation operation. The amount of charcoal to be added to the secondary circuit will vary with the treatment of different ores, but satisfactory results have been obtained in the treatment of many ores with 1 lb. of charcoal per ton of ore.

## Complexity of Double-stage Treatment

The complexity of the double-stage process is not as serious as might appear in that the required time of agitation of the secondary charcoal with the ore pulp is relatively short and the charcoal is floated very rapidly from the ore pulp.

## Amounts of Charcoal

In the treatment of low-grade tailings satisfactory adsorptions have been obtained with 2 lb. of charcoal per ton of tailing. With higher-grade materials assaying up to 0.40 oz. gold per ton, 3 to 7 lb. of charcoal per ton of ore have been found satisfactory providing the double-stage process is employed.

## Pulp Densities

The ratio of solids to solution permissible is limited only to the requirements for satisfactory agitation and flotation operations. As far as adsorption is concerned, better results have been obtained in thick pulps than in thin. The equilibrium encountered in adsorption appears to be a function of concentrations of gold in the charcoal and solution; this being the case, it appears desirable to permit the simultaneous dissolution and adsorption to proceed in pulps of maximum allowable pulp densities.

## Strength of Cyanide

Since the only method of recovering cyanide is by means of a thickener placed after the final flotation operation, it follows that the cyanide in the thickener discharge is lost unless further reclamation is obtainable from a tailing pond. With an ore adapted to countercurrent cyanide methods, the tailing pulp discharged would not contain more than 1.5 tons of solution per ton of solids and the normal pulp discharged would probably be nearer 1 ton of solution per ton of solids. Since the simultaneous dissolution and adsorption process has been suggested by the writer to have possibilities in the treatment of ores of slow settling rates it follows that in the treatment of such ores it will be necessary to discharge more dilute pulps ranging from 1 ton of solution per ton of solids to as high as 3 tons of solution per ton of solids, and that in consequence it is essential to dissolve the gold from such ores with very low cyanide strengths in order to avoid excessive losses of cyanide. Fortunately, ores of the class mentioned usually require but low cyanide strengths and typical cyanide strengths at the end of simultaneous dissolution and adsorption which have been found to yield satisfactory recoveries with many such ores range from 0.003 to 0.010 per cent, or from 0.06 to 0.20 lb. of sodium cyanide per ton of solution. In considering the finishing strength of cyanide following agitation, a process based on simultaneous dissolution and adsorption has one possible advantage over current cyanide methods in that "premature precipitation" sometimes encountered with current cyanide methods is not likely to occur, since the gold is adsorbed as rapidly as dissolved and once adsorbed is not likely to migrate from the charcoal under normal conditions.

## Flotation of Activated Charcoal

Under favorable conditions, it has been found that properly conditioned activated carbon may be rapidly floated as compared to the flotation of sulphides from ore pulps. The writer estimates that the capacity of a given mechanical subaeration flotation unit would be about three times as great in floating charcoal as compared to floating sulphides from an ore classed as average. In floating charcoal from ores containing sulphides no difficulty, except in one instance, was encountered in depressing sulphides. In certain cases where it appears desirable to float sulphides with the charcoal, encouraging results have been obtained in the laboratory, but a definite statement covering all conditions cannot be made because each ore must be tested separately to determine the results. The carbon contents of cleaned flotation concentrates produced in the laboratory in tests ranging from 75 to 300 lb. of ore varied from 28.8 to 82 per cent. The low figure was obtained in treating an ore containing a small amount of an unidentified gangue mineral, which persisted in floating with the charcoal.

## Recovery of Silver

The simultaneous dissolution and adsorption process in its present form is not, in the writer's opinion, adapted to the treatment of silver ores. Small amounts of silver soluble in cyanide occurring in gold ores are recovered and silver not soluble in cyanide may under certain conditions be recovered by flotation when the charcoal is floated, but on the whole the process is not attractive for the treatment of ores containing appreciable amounts of silver soluble in cyanide.

## Treatment of Charcoal Product

The possibilities of disposing of the charcoal flotation concentrate are: (1) shipping directly to a custom smelting plant; (2) burning the carbon, briquetting and shipping the resulting ash to a smelting plant; (3) cyanidation of the ash by the simultaneous dissolution and adsorption process in order to raise the grade of the ash so that bullion may be produced by melting.

## Results of Ore Tests

Results of laboratory tests by the single-stage and double-stage processes are given in Table 2 for samples ranging from 75 to 300 lb. The

TABLE 2.—*Results of Ore Tests*

| | Weight, Lb. | Tons per 100 Tons of Material Treated | Assays, Oz. Gold per Ton | Per Cent |
|---|---|---|---|---|
| *A.*—OVERFLOW OF WASHING PLANT FROM PHILIPPINE ISLANDS | | | | |
| Heads | 104.9 | 100.0 | 0.038 | 100.0 |
| Primary charcoal ash | 0.01822 | 0.01736 | 113.60 | 51.9 |
| Secondary charcoal ash | 0.02119 | 0.02019 | 41.25 | 21.9 |
| Combined charcoal ash | 0.03941 | 0.03755 | 71.17 | 73.8 |
| Primary barren solution | 419.6 | 400.0 | 0.0003 | 3.2 |
| Secondary barren solution | 524.5 | 500.0 | tr. | |
| Tailing | 104.9 | 100.0 | 0.010 | 26.2 |
| *B.*—SLIME PORTION OF CYANIDE TAILING FROM MEXICO | | | | |
| Heads | 300.0 | 100.00 | 0.034 | 100.0 |
| Primary charcoal ash | 0.1816 | 0.0605 | 38.40 | 68.3 |
| Secondary charcoal ash | 0.0615 | 0.0205 | 6.55 | 4.0 |
| Combined charcoal ash | 0.2431 | 0.0810 | 30.34 | 72.3 |
| Primary barren solution | 600.0 | 200.0 | 0.00015 | 0.9 |
| Secondary barren solution | 1200.0 | 400.0 | tr. | |
| Tailing | 299.76 | 99.92 | 0.0094 | 27.7 |
| *C.*—SLIME PORTION OF AMALGAMATION TAILINGS FROM MONTANA | | | | |
| Heads | 118.62 | 100.0 | 0.102 | 100.0 |
| Primary charcoal ash | 0.3593 | 0.3029 | 22.65 | 67.1 |
| Secondary charcoal ash | 0.2035 | 0.1716 | 12.33 | 20.6 |
| Combined charcoal ash | 0.5628 | 0.4745 | 18.92 | 87.7 |
| Secondary barren solution | 532.3 | 448.7 | 0.0006 | 2.6 |
| Tailing | 118.06 | 99.53 | 0.010 | 9.7 |
| *D.*—LOW-GRADE SLIME PRODUCT FROM CALIFORNIA | | | | |
| Heads | 150.0 | 100.0 | 0.046 | 100.0 |
| Primary charcoal ash | 0.598 | 0.399 | 10.30 | 88.5 |
| Secondary charcoal ash | 0.208 | 0.139 | 1.11 | 3.3 |
| Combined charcoal ash | 0.806 | 0.538 | 7.92 | 91.8 |
| Primary barren solution | 225.0 | 150.0 | 0.00058 | 1.9 |
| Secondary barren solution | 600.0 | 400.0 | 0.00015 | 1.3 |
| Tailing | 149.2 | 99.46 | 0.003 | 6.9 |
| *E.*—ORE FROM PHILIPPINE ISLANDS | | | | |
| Heads | 73.48 | 100.00 | 0.287 | 100.0 |
| Primary charcoal ash | 0.0731 | 0.0995 | 207.85 | 72.0 |
| Secondary charcoal ash | 0.0728 | 0.0991 | 49.00 | 16.9 |
| Combined charcoal ash | 0.1459 | 0.1986 | 128.58 | 88.9 |
| Primary barren solution | 147.00 | 200.00 | 0.0126 | 8.8 |
| Secondary barren solution | 235.14 | 320.00 | 0.0006 | 0.7 |
| Tailing | 73.33 | 99.80 | 0.030 | 10.4 |

equipment used comprised a 30 by 30 inch Turbo Agitator, a five-cell continuous Denver laboratory flotation machine and a 45 by 28 inch settling tank.

Treatment by the single-stage process consisted in agitating the ore pulp with lime, cyanide and activated charcoal, after which the charcoal was conditioned with reagents and floated. The rough concentrate was cleaned in a laboratory batch 2000-gram capacity Denver flotation machine.

Treatment by the double-stage process comprised the single-stage treatment as described followed by agitating the tailing pulp and thickened cleaner middlings with fresh charcoal. After agitation the charcoal was removed by flotation and the charcoal concentrate cleaned as previously described.

The results given in Table 2, sections *A*, *B*, and *C*, were obtained on material not considered amenable to treatment by countercurrent decantation or filtering methods. In each of these tables the primary charcoal product represents the result of the single-stage treatment and the combined primary and secondary charcoal products represent the result of double-stage treatment.

Additional data including amounts of charcoal used, strengths and consumptions of lime and cyanide, pulp dilutions, and time of agitation, are given in Table 3.

TABLE 3.—*Data for Tests Given in Table 2*

| | A | B | C | D | E |
|---|---|---|---|---|---|
| Charcoal used, lb. per ton of ore treated: | | | | | |
| Primary stage | 2.0 | 4.0 | 4.0 | 4.0 | 4.0 |
| Secondary stage | 1.0 | 2.0 | 1.0 | 1.0 | 1.0 |
| Lime, lb. per ton of ore treated | 14 | 4 | 14 | 9 | 6.5 |
| Lime in solution after primary agitation, lb. per ton | 0.056 | 0.190 | 0.090 | 0.250 | 0.112 |
| Dilution for primary agitation, tons solution to solids | 3 | 2 | 2.42 | 1.5 | 2.0 |
| Cyanide consumption, lb. per ton of ore treated: | | | | | |
| Chemical | 0.20 | 0.23 | 1.73 | 0.30 | 3.48 |
| Discharged in pulp, assuming 3 to 1 dilution | 0.48 | 0.29 | 0.19 | 0.45[a] | 0.35[a] |
| Total | 0.68 | 0.52 | 1.92 | 0.75 | 3.83 |
| Strength of cyanide after primary agitation, lb. per ton of solution | 0.20 | 0.20 | 0.20 | 0.78[b] | 0.35 |
| Primary agitation, hr | 12 | 7 | 15 | 8 | 22 |
| Secondary agitation, hr | 3 | 3 | 4 | 2.5 | 4 |
| Percentage of carbon in primary concentrate after cleaning | 80 | 78 | 30.5 | 32.1 | 62.1 |
| Percentage of carbon in secondary concentrate after cleaning | 77.4 | 82 | 36.2 | 28.8 | 41.9 |

[a] Pulp discharged with 40 per cent solids.

[b] Higher than necessary.

## REFERENCES

1. J. Gross and J. W. Scott: Precipitation of Gold and Silver from Cyanide Solution on Charcoal. U. S. Bur. Mines *Tech. Paper* 378 (1927). Contains a bibliography.
2. J. V. N. Dorr: Cyanidation and Concentration of Gold and Silver Ores, 206. New York, 1936. McGraw-Hill Book Co.
3. Julian and Smart: Cyaniding Gold and Silver Ores, Ed. 3, 123. Lippincott Co.
4. E. M. Hamilton: Manual of Cyanidation, Ed. 1, 121. New York, 1920. McGraw-Hill Book Co.

## DISCUSSION

*(E. W. Engelmann presiding)*

C. E. LOCKE,* Cambridge, Mass. (written discussion).—Dr. Chapman's process seems to offer an easy solution for the problem of treating certain types of difficult gold ores by the cyanide process.

I appreciate that the process has not been in commercial operation long enough to afford any reliable cost data, but perhaps Dr. Chapman can give some general figures on costs, particularly in comparing cost of his process with cost of the usual cyanide operations.

No mention is made of the nature of the charcoal that he recommends for use, the fineness to which it should be ground, and the technique of activating it. Also, was there any loss in the procedure of drying and burning the floated charcoal, which is a rather light material and, especially for rich ores, might be a very valuable product, which would have to be handled carefully in order to avoid loss by dusting or during combustion. Just what type of furnace combustion procedure does he recommend for handling the charcoal?

On page 218 the statement is made that the ash may be treated by his process just as the original ore is treated. Has he accumulated any data showing that this method is feasible and, if so, what results have actually been obtained?

T. G. CHAPMAN (written discussion).—I am sorry that I cannot furnish any specific data regarding a comparison of costs of the proposed process with that of usual cyanide operations. With respect to the initial cost of plant, such estimates as are available indicate a substantial saving in favor of the proposed process, especially if the single-stage process is compared with current cyanide plants. As stated, operating costs are not available and such computations as have been made show about the same operating costs as with current methods. In the paper, I did not propose that my process in its present state of development would compete with current cyanide methods, but did propose that the process offered promise in treating certain ores and tailings, which for one reason or another could not be profitably treated by current methods. The main reason for not proposing that the process could compete with current cyanide methods is the lack of operating data and cost data for the process in question.

I find that charcoal made from pine stumps is satisfactory after activation for adsorption of gold. I have been using charcoal furnished by the Southern Pine Chemicals Co., of Jacksonville, Florida. This charcoal is available at a cost of $20 per ton f.o.b. San Pedro. Charcoal breeze is also satisfactory and can be purchased at a lower rate. The charcoal is dry-ground to 150-mesh, heated to 1450° F. for at least 30 min. after this temperature is reached, and cooled as rapidly as possible.

---

* Professor of Mining and Ore Dressing, Massachusetts Institute of Technology.

Experimental work shows that charcoal so prepared retains its adsorptive properties for weeks, if not months. It is not claimed that activated charcoal prepared in this manner has the high adsorptive degree of the manufactured activated carbons, but considering the cost of such carbons I believe that charcoal prepared in the manner described, costing approximately 2¢ per pound, is superior. The manufactured carbons as prepared for the market are usually ground too fine for satisfactory flotation, although I suppose that this difficulty could be overcome by preparing a manufactured charcoal as a coarser product.

As to methods of burning the carbon and the possibility of dust losses due to handling, it should be pointed out that it is difficult to give as much information on these points as on the other phases of the process because of the difficulty of obtaining sufficient amounts of gold-bearing charcoal to test the proposed procedures on a large scale. I have, however, during the past six months made synthetic mixtures of slime and ground charcoal for the purpose of determining a proper method of burning the carbon, and after experimenting with reverberatory-type roasting furnaces, downdraft equipment, and the brazier type of burner, I have come to the conclusion that the brazier is the proper method of burning finely divided charcoal containing from 20 to 75 per cent of slime. The brazier was investigated by H. R. Edmands, who reported the results of his work in *Transactions* of the Institution of Mining and Metallurgy, London, 1918, page 289.

Edmands burned pure charcoal obtained by treating clear solutions, whereas the present problem is to burn charcoal containing considerable amounts of slime. The procedure recommended is to break up the filter cake, which contains about 30 to 35 per cent moisture, into 2-in. lumps. Heavy iron boxes having screen bottoms, each approximately 16 by 16 by 16 in., are used. Live coals are placed on the screen and the wet filter cake is placed on the live coals. These boxes are then placed in a steel cabinet equipped with holes at the bottom and top for the passage of air and gases of combustion, respectively. Slow combustion takes place without use of additional fuel and apparently without dust losses. Furthermore, the presence of slime aids this operation in that the form of the lumps is more or less retained, especially if the carbon content is not too high. Although the operation is somewhat slow, when it is considered that additional fuel is not required, that attention is not required, and that the first cost of the equipment is exceedingly low, I believe this method will prove practical.

Professor Locke refers to a statement relating to the treatment of ash by the charcoal process in order that its grade be raised. I have experimental data that indicate that this can be done, and the advantage of using such a method would be that a small amount of carbon left in the residue after burning would not affect such a process, whereas any carbon left in the ash would affect normal cyanide methods. Although it will take approximately 100 lb. of carbon per ton of ash to re-treat the ash, assuming that the ash assays approximately $5000 per ton, it will not be necessary to purchase new carbon for this purpose, since the carbon may be taken from the cleaner flotation cells of the main plant.

E. L. Sweeney,* Denver, Colo. (written discussion).—I will discuss this paper only from the design and construction viewpoint. Probably the greatest application of this process will be on ores or tailings, that are hard to wash, either by the use of thickeners or filters. The cost of the installation of a large group of thickeners or filters is high per ton of ore to be treated, especially in colder climates where tankage must be housed. I have analyzed plants that I have erected, those using the countercurrent decantation method and those using the combination of C.C.D. and filters.

---

* Consulting Metallurgical Engineer and Contractor of Plants for Mines.

I believe that when the Chapman process will fit the ores to be treated, the installed cost of the plant can be cut from 30 to 50 per cent, depending upon whether it is in a mild or cold climate.

A natural question would be: How is it possible to cut the amount of washing needed in comparison with the amount of washing necessary in a standard cyanide plant? From various discussions I have had with the writer of this paper, as well as observations obtained in test runs, I am convinced that a much lower cyanide content can be carried in the solutions, therefore less washing will be needed to recover free cyanide; also, that the gold will be adsorbed on the charcoal so quickly that the amount of gold in solution in the flotation tailings will be very low.

L. B. EAMES,* Deadwood, S. D. (written discussion).—Two conditions with which I have had experience may be of interest in considering Dr. Chapman's paper. At the Goldfield Consolidated mill, the pulp passed continuously through a series of 10 Pachuca tanks. Pulp taken from the last of these and reagitated in bottles without change of solution showed no further extraction over a period of from 24 to 48 hr., but a sample taken from the Butters filter leaves just before discharge would readily yield 0.02 to 0.03 oz. additional gold extraction. It is possible that a material increase in recovery might have been realized had Dr. Chapman's process been available.

On the other hand, in the small operation now being conducted by The Canyon Corporation, where blue ores are being roasted and cyanided with countercurrent washing, dissolving continues throughout the washing process. This gives a much longer contact than would be realized in the adsorption flotation procedure and much gold that is now recovered might be lost by its use. In spite of the continued dissolving, the wash recovers over 99.5 per cent of the metal dissolved.

---

* Manager, The Canyon Corporation.

# Milling Developments at the Benguet Consolidated Plant

By J. M. Morris,* Member A.I.M.E.

(San Francisco Meeting, October, 1935; also New York Meeting, February, 1936)

The point to be made most clear in this paper is the economic value of flotation in the Benguet mill flow sheet. It is rather a statement of effect with no attempt at a technical explanation of the cause. Certain well-known, easily understood reagents, mechanisms and principles have been adapted to the conditions at Benguet, and have proved to be more successful than was demonstrated in the laboratory.

The mechanical and metallurgical development of this particular operation was arrived at by trial and error, with fortunately very little error. Changes were slow, of necessity, which in the end proved a blessing in that time was afforded for observation and analysis of the disturbing factors; and as a result each change was a definite step towards higher efficiency. Many of these steps were unpredictable from laboratory work because of the varied and differing characteristics of ores met with in daily operation of the mill, which were practically impossible to reproduce on a laboratory scale.

The Benguet mill receives daily ores that differ as much as if they were delivered from three different properties. There is first the surface and upper-level zone, which produces an oxidized secondary ore containing considerable iron oxide, manganese oxide and some organic matter. Formerly, most of this ore consisted of very soft fill with some hard rock mixed in. It also contained an unusual amount of iron and aluminum sulfate, which formed hydrates upon entering the alkaline cyanide solution and caused excessive frothing.

When flotation was introduced in the Benguet mill the general characteristics of this upper-level ore had changed considerably, in that it was practically all newly mined, fairly hard ore. It still contained many of the same disturbing elements, but was somewhat simpler to treat than formerly. The small proportion of fines is still troublesome in flotation, and plant practice probably does not show more than 80 per cent extraction on this small portion of the ore. No definite figure on this is available, as this particular ore is delivered at irregular intervals

---

Manuscript received at the office of the Institute Oct. 3, 1935. Issued as T. P. 675, February, 1936.

* Mill Superintendent, Benguet Consolidated Mining Co., Manila, P. I.

and in irregular quantities, so the assumption of 80 per cent is based on rather sketchy laboratory work plus daily observation of flotation performance.

The second type of ore is mined between the 100-ft. and 400-ft. levels and collected in pockets and hoisted from the 500-ft. level. This is a mixture of primary and secondary ore containing very little oxide. In general it is fairly soft, showing considerable kaolinization and clay with a large percentage of fines, some of it running more than 22 per cent minus 100-mesh. This ore is fairly simple to treat by flotation, providing the slime is well washed and a sufficient dilution is maintained to disperse all the slimes. Neither starch nor sodium silicate seems to be of special benefit in its flotation, but the pulp must be maintained on the acid side. Should the pulp become alkaline the froth forms in large, slimy bubbles and the extraction drops rapidly as the alkalinity increases to some indefinite point. However, on the other hand, laboratory work shows

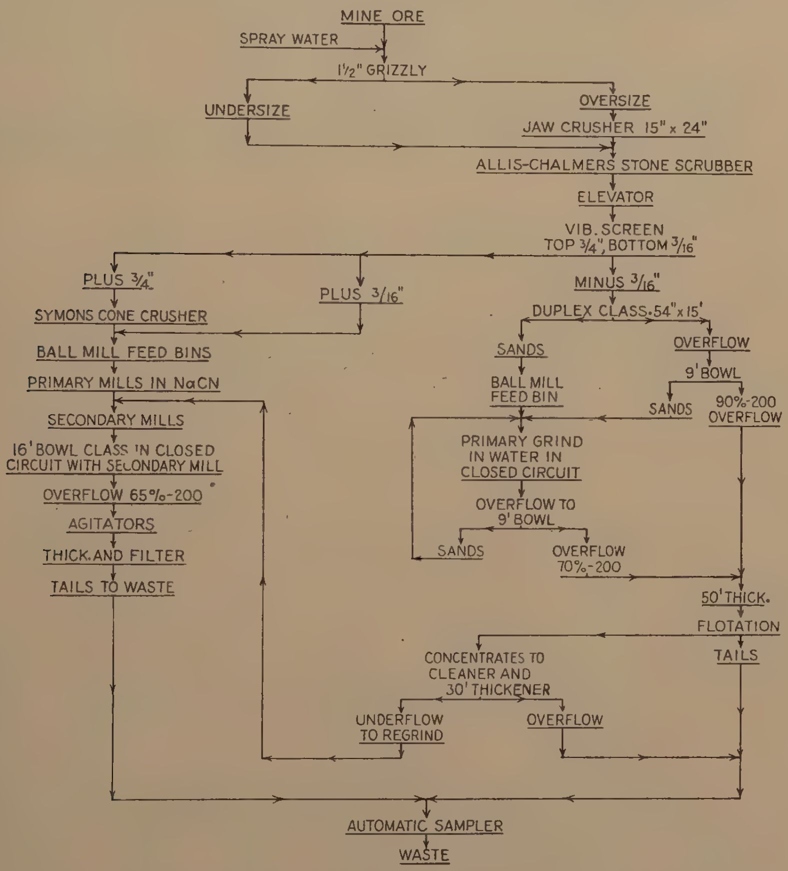


Fig. 1.—Flow sheet of mill, Benguet Consolidated Mining Co.

that almost as good extraction from this special ore can be made in an alkaline circuit, using lime as the reagent, but the ratio of concentration is much lower, producing an extremely dirty, uncontrollable froth. Sodium carbonate may be used also, with slightly lower results, and produces a low-grade, dirty concentrate.

The third type of ore is from the 500 to 700-ft. levels, collected and hoisted from the 700 and 750 levels. This is a fairly hard, clean, primary ore, containing very few slimes, perhaps not more than 4 or 5 per cent minus 100-mesh. This figure is not conclusive and is based on the screening of a few grab samples. This seems to be a fairly ideal flotation ore and extraction is good on the natural slimes, probably averaging from 94 to 95 per cent.

The quantity of these different ores delivered daily to the mill varies, and as a result the quantity of the primary slimes coming to the flotation unit also varies; so when flotation was first started it was very difficult to anticipate how much slimes it would be necessary to handle from day to day. But later this trouble was remedied by the installation of a 50-ft. thickener, which absorbed the surges, therefore we have now arrived at a fairly close estimate of the fines on the total ore over a period of several months. These natural slimes amount to about 12.5 per cent of the total ore.

Owing to the fact that the mine is working in many separate ore-shoots where the products may change in value from day to day, it would be extremely difficult to maintain an even head and at the same time a uniform delivery as to the type of ore. As a uniform head was desired at all times, the mine had to deliver the ore according to value regardless of type. So it was necessary that the mill absorb these changes and in this flotation has proved invaluable, in that practically all the surge of fines is absorbed by the flotation unit, leaving only clean sized rock for the milling unit, permitting a constant feed of a fairly uniform material, and tonnage variation is practically controlled by the hardness of the ore, while the flotation feed at the cells is fairly constant after having been collected in the surge thickener.

Formerly in straight cyanidation part of the slimes was washed out of the ore by cyanide solution and as a result when ore was being hoisted an excessive amount of slime material went to the classifier circuit in a series of very irregular surges. Milling operations under these conditions would be rather difficult.

In general the Benguet ore may be described as a mixture of quartz, andesite, altered diorite, iron oxide and sulfide, and clay. G. O. Scarfe described the mineralization as follows:

> The gold occurs in a finely divided state, associated with pyrite, marcasite, a little tetrahedrite, and a little galena, and a gangue of fine grained cryptocrystalline quartz, sometimes showing rhodochrosite. Tellurides are probably present, although none

> were recognized. The brown color of some of the gold suggests their occurrence. Calcite is conspicuous by its scarcity, while the deposit is unique because of its association with large masses of anhydrite. Crystallized gypsum frequently occurs, usually imbedded in quartz.

The presence of tellurium in the Benguet ores has always been accepted and various analyses on concentrates and precipitates have definitely shown it to be present.

In 1930, A. D. Alvir, of the Bureau of Science at Manila, published a paper on Antamokite, a New Gold-silver Telluride. This classification was made on ore from the "153 west vein on the E level of the Antamok mine." Mr. Alvir says in part:

> The mineral occurs in very tiny portions always associated with calaverite in the ore. Consequently it was almost impossible to isolate it for chemical analysis. However, after a long search, slightly larger portions of it were found, essentially free from calaverite. These were gouged out with a needle, and analyzed. There was not enough for a thorough chemical analysis, but what there was showed gold, tellurium and traces of silver. No lead, antimony or copper was found, showing that in all probability it is a gold telluride with a little silver. This mineral, quite conclusively a new species, is hereby named Antamokite, after Antamok.

Whether or not Mr. Alvir was justified in naming a new mineral in this case is a matter for others more capable of judging than the present author, but that he isolated and showed telluride is conclusive. The polished sections used by Mr. Alvir in making his classification certainly show a difference in the appearance of the telluride minerals. In accepting the fact that tellurides are present there has been a tendency to lay more tailing loss to their presence than is warranted. In 1920, Clyde M. Eye, General Superintendent, and M. E. Dodd, Mill Superintendent, wrote an article for the *Mining and Scientific Press*, in which they said:

> From the time the ore enters the mill until it is discharged is about seven days, which should be ample for the complete dissolution of the precious metals, were it not for the fact, well established by experimentation, that there is a definite amount of gold and silver in combination with tellurium. Repeated experiments on the tailing discloses the fact that the slimes portion (finer than 200 mesh) contain the major part of the undissolved metal and that, whereas the concentrate from the tailing stream has a value of $30.00 per ton, the percentage represented by this is so small as to account for considerably less than half the loss. It is evident, therefore, that it is mainly due to the presence of a very finely disseminated high-grade mineral with the gold and silver in combination, so that concentration offers no remedy. Flotation experiments have been made on the tailing with indifferent results.

To a greater or less degree, the same conditions existed until 1934. Most of the tailing loss was attributed to the presence of tellurides until late in 1933, when a sample of tailings was sent to the American Cyanamid Co. to determine the nature of the gold losses. The specific information desired was: (1) gold and silver assay on tail; (2) screen tests of tailing with assay of each screen product; (3) microscopic examination of the tailing to establish positively the form in which the gold occurs.

After conducting the necessary experiments the American Cyanamid Co. summarizes its findings as follows:

> The result of our test work indicates that the principal losses in the Benguet tailings were in the form of gold associated with pyrites. It is such that the losses might be reduced by the adoption of:
>
> (*a*) Finer grinding of the ore to release sulfides from the gangue,
> (*b*) Finer grinding of the pyrite itself by means of improved classification and selective grinding,
> (*c*) Flotation of the cyanide tailing followed by regrinding and cyanidation of the pyrite concentrate,
> (*d*) Longer time of contact during cyanidation.

About this time a series of flotation and concentration tests were being made on the tails at Benguet, and samples of the finer concentrates made in these tests and examined locally under a high-powered microscope proved to be practically all pyrite. By dissolving some of this pyrite, microscopically fine gold threads were identifiable; therefore, I am convinced that the tellurides in the Benguet ore are practically negligible as a source of loss, and that the greater losses are due to the extremely fine mechanical association of the gold with the pyrite. Some gold is still tied up in the pyrite at minus 325 mesh. This loss apparently is being remedied in a small measure by the present practice of flotation of the primary slimes, sending the concentrate to regrind.

Any discussion of the development of flotation in the present milling practice at Benguet would not be complete without a very thorough review of the history of the milling operation since its inception in 1906. As complete records are not available, only experimental work of which there are records will be cited, which very definitely show that what is being done now is merely what was indicated when the plant first started, long before flotation was considered as a possible means of gold extraction. The need for some special treatment of slimes is shown in the article previously mentioned (*Min. & Sci. Pr.*, Dec. 4, 1920). With reference to the plant practice in 1906, Mr. Eye says in part:

> The initial recovery made by this plant on fairly well oxidized ore from near the surface was poor, but even at that was better than anything that had been done in the islands up to that time. About one-third of the gold was caught by amalgamation, and of the gold in the sand about 70 per cent was recovered by leaching. It soon developed, however, that the slimes overflowing the classifier (sent to waste), and amounting to nearly 40 per cent of the ore, was of better grade than the sands (even at times exceeding in value per ton the original ore). This naturally led to the introduction of slimes treatment.

He speaks further of the difficulties of settling, thickening, tail losses, etc., which could very well describe the present plant up to the starting of the flotation. As a matter of fact, improvements in plant practice with regard to cyanidation made during the last 18 years have been mostly mechanical, with the exception of precipitation. In other words, colloidal slimes interfered with thickening and filtering, requiring excessive tankage, and resulting in indeterminable losses for 18 years while flotation was being developed in the base-metal plants and later adapted to gold extraction. And now that flotation is a regularly incorporated unit in the plant, it is so simple and so cheap that it seems unreasonable that we should have gone so long without it. But in looking back over the experiments during the past 12 years, right down to the most recent work, it is readily evident that experiment was disheartening and actual plant practice has proved to be many times more successful and beneficial than experiment ever indicated.

Records of flotation experiments on Antamok ore go back as far as 1917 or 1918; then again in 1921, the year in which the first xanthates, at that time called specific organic collectors, were invented, ore samples were sent to the United States for flotation tests. These tests showed extractions of from 86 to 94 per cent, which should seem very encouraging, but the quantity of reagents used at that time made the costs prohibitive; in fact, in some cases exceeded the value of the ore. To quote from early conclusions and recommendations:

> 1. There would be nothing gained by using flotation at any stage in the treatment of the Benguet ore at the present time, nor at any time in the future, unless the losses in cyanide residue increase or the opening of lower levels in the mine discloses ore carrying copper, zinc, and antimony in amounts sufficient to interfere seriously with cyanidation.
> 2. Flotation of the raw slimes yields a high (93 per cent) extraction in a good grade ($344) concentrate, but the cost of producing and disposing of the concentrate would reduce the actual recovery to a point considerably below that obtainable by direct cyanidation.

The results of these experiments gave no encouragement whatsoever; and there the matter stood for about 10 years.

In 1931, E. N. Bagley became mill superintendent, and in November of the same year instituted a series of flotation tests. These tests were all conducted on the entire ore and as they did not prove very encouraging were discontinued early in 1932. In 1933, a complete assortment of new flotation reagents was received and a new series of experiments was conducted on the ore, tails and primary slimes. These tests were far more encouraging with the new reagents; and because slimy ore seemed to be increasing, causing more and more trouble in the plant, flotation was looked on with more consideration than before. An experienced flotation laboratory man joined the staff and conducted another series of experiments, which bore out previous results. Even with these encouraging results it still seemed very much of a gamble and no definite action was taken. In September of 1933, Mr. Bagley was transferred to Balatoc, and upon leaving reported to the management as follows:

In an effort to decrease the tailing loss at the Benguet Consolidated mill, three lines of action which have promising possibilities are presented.

Method No. 1 is to bulk float the sulfides in the tails, roast the concentrates to produce sulfuric acid, which is required to successfully float the sulfides in the cyanide plant tailing, and then return the roasted concentrate to the plant for cyanidation. This line of action was suggested by the fact that a considerable amount of gold lost in the tailings is associated with the sulfides in such a way as to make a high recovery by direct cyanidation extremely difficult. The amount of sulfides in the ore treated has increased from about 3 to about 10 per cent in the past two years.

Method No. 2 is to use water at the mine elevator instead of cyanide solution. Then float the free gold and sulfides in the slimes after washing, screening, and classification. As water would be used in this method, the tailing from the flotation cells would have to be sufficiently low in value to be discarded as plant tailings.

The concentrate from the cells would be run to the grinding circuit to be ground with the ore or in a separate mill for extremely fine grinding, as may be most desirable. The object of this method is to keep the primary slime from entering the cyanide plant, thereby increasing the capacity of the cyanide department and minimizing the frothing. The elimination of soluble salts in the primary slime should also reduce cyanide and lime consumption and also increase extraction by minimizing fouling of plant solutions.

Method No. 3 is to use water at the mine elevator and classify the screen undersize as in method No. 2. Then run the classifier dragover to the regrinding mills, and the classifier overflow to No. 2-A thickener. As no cyanide solution would be present in the pulp up to this stage of the process, the thickener overflow would be run to waste. The partially dewatered pulp as thickener underflow would then go to a filter for further washing and dewatering. The filter effluent would be run to waste and the filter cake repulped in mill solution and pumped to the primary thickeners.

The object of this method is to water wash the primary slimes to remove the soluble salts which cause frothing in the plant, and which consume cyanide and lime and cause fouling of solutions.

All this work on flotation was timely, because a desperate stage had been reached, where something had to be done to relieve the plant of slime and froth. Furthermore, the increased price of gold had increased the ore reserve considerably, so that the logical procedure was to mine a lower head and mill larger tonnage; and by installing a new classifier and by building up larger circulating loads in the grinding circuit at least 200 tons more grinding capacity could be made available if the mill was willing to take a little less extraction for the sake of the greater tonnage. The mine was in a position to deliver 700 tons per day, but the cyanide plant was badly overloaded with 500 tons per day, and there was no room for expansion. Work was continued on the primary slimes angle, which seemed the most promising way out of the difficulties, with encouraging but not entirely conclusive results, and finally an expenditure of about ₱4,000.00 was authorized for a small home-made plant. This plant, consisting of a 10 by 12-ft. agitator, two home-made pneumatic cells, half a dozen tin cans and a lot of hope, was started in January, 1934, and the immediate results were so favorable that the entire cost of the plant was more than returned in the first few weeks of operation. Almost immediately the construction was started of a 50-ft. thickener as a surge tank for the flotation feed; then two mechanical cells were installed on approval; and later, four more were purchased. Recently one of the primary cyanide thickeners has been taken over from the cyanide circuit to thicken the concentrates. And at the present writing the flow sheet of the Benguet mill is so very simple as to be almost foolproof and requires very little detailed description.

The ore as delivered from the mine is dumped directly to a 1½-in. grizzly, where water sprays are played on it, the fines passing the grizzly and the coarse ore force fed into a 15 by 24-in. Traylor jaw crusher, the crusher product joining the fines in a feed chute to a 6 by 10-ft. Allis-Chalmers stone scrubber where all the clay is reduced to slimes. The scrubber discharges to a bucket elevator, which delivers the scrubber discharge (ore, water and slime mixture) to a 3 by 8-ft. Allis Chalmers centrifugal vibrating screen equipped with ¾-in. top screen and 3⁄16-in. bottom screen. The plus ¾-in. ore drops direct into the Symons-crusher surge bin, the minus ¾-in., plus 3⁄16-in. material is conveyed to the ball-mill feed bins and the minus 3⁄16-in. and slimes run in a launder to a Dorr 54-in. by 15-ft. Duplex classifier. The dragover from this classifier discharges directly into a bin for fine mill feed, of 281 tons capacity, while the overflow goes to a 9-ft. bowl classifier. The dragover of this classifier goes to the fine-grinding section sand distributor, while the overflow, averaging 90 per cent minus 200-mesh, flows to a 50-ft. thickener used as a surge tank for the flotation feed.

As this slime will not settle or thicken to any great extent, a constant feed is maintained to the flotation unit, which pulls the thickener low when no ore delivery is being made and allows it to fill up when ore is being delivered. This system eliminates any surges in the plant and the operation may run for days without any major adjustment unless the ore changes radically. The underflow of the 50-ft. thickener is raised by a Dorrco duplex diaphragm pump discharging into a 10 by 11-ft. Dorr agitator where approximately 0.05 lb. per ton slime of an organic collector is added and sufficient sulfuric acid to maintain a pH of between 6.6 and 6.8. As the mine water is acid, with certain supplies carrying an acidity as high as a pH of 5.2, very little extra acid is ever needed. The conditioned pulp flows by gravity to the primary flotation cells, where pine oil at the rate of 0.2 lb. per ton of solids is added. The tails from these cells flow through a secondary bank and the tails from the secondary cells are sent to waste. Because of the large volume of froth that it is necessary to pull, a cleaner cell has been introduced on the concentrates, which so far has resulted in a higher average concentrate, but also a higher tail. However, the plant is generally benefited by the reduction of the volume of water that enters the cyanide circuit with the flotation concentrates. Various attempts at thickening and filtration have proved unsuccessful because much of these concentrates is of a colloidal nature. Attempts at filtration have resulted in an extremely thin, gelatinous cake with from 3 to 5 per cent of the solids running from $40 to $50 per ton pulling through the filter media. Various methods of handling concentrates are being investigated and no doubt a system much more satisfactory than present practice will be found. Experimental work is continuing in an attempt to generally refine the practice, now that there is a certainty that its application is practical.

The thickened concentrates are fed to the concentrate stream, entering the 6 by 10-ft. pebble mill, where they are probably all reduced to less than 300 mesh.

The cells and reagents require very little attention, but occasionally it is necessary to add or reduce the acid according to the pH. The Lamotte block set and indicators are used for determining the pH, although this may be judged very closely from the appearance of the froth.

Flotation tails are hand-sampled at the cell discharge but join the cyanide-tails launder at the Oliver filters, where another sample is taken by an automatic sampler, which is used as a combined mill tails.

The cyanide-plant grinding unit reduces the ore to between 60 and 70 per cent minus 200-mesh, where it enters the slime plant, which consists of primary thickeners, primary agitators, secondary thickeners and secondary agitators, with a third and fourth set of thickeners giving about 65 hr. contact at the present rate of 770 tons per day. Filtering is performed on four 12 by 18-ft. Oliver filters. It is interesting to note that the life of a filter cover averaged about three months before removal of the primary slimes and now averages better than five months. Furthermore, three filters handle the increasing tonnage, while with the slime in the ore four filters were crowded at around 500 tons. Solution in the grinding circuit and primary thickeners is maintained at NaCN 1.34 and CaO 1.34 lb. per tons. All cyanide and lime are added in the grinding circuit. The Merrill-Crowe scheme of precipitation is used.

## SUMMARY

A general summary of the benefits derived from flotation in the flow sheet of the Benguet mill may be stated as follows:

1. Total plant increased from 500 to 770 tons per day, with no increase in tankage in the cyanide unit.
2. Froth considerably less than on the 500-ton basis, with absolutely no slime losses through frothing.
3. Filter life and filter efficiency almost doubled.
4. Solution pump troubles ended; and pump life quadrupled.
5. Milling costs reduced more than 25 per cent, a saving that more than offsets the loss in extraction.

The capital costs of increasing the plant from 500 to 770 tons per day with flotation was less than one-fourth the cost of increasing the all-cyanide plant from 300 to 500 tons. This cost includes certain pieces of equipment that were purchased and installed before flotation was started, and while this equipment was not being used to its full efficiency in the cyanide plant on a 500-ton basis, it was necessary for the increased tonnage, so that is charged out to flotation. Otherwise the increase of from 500 to 770 tons per day would not have amounted to more than one-tenth the cost of increasing the plant from 300 to 500 tons all cyanidation. At 770 tons we are able to maintain clear solution overflows on all thickeners. Precipitation is regular at all times and the operation in general much smoother, requiring less supervision and maintenance than at 500 tons all cyanide; and while at first flotation seemed to be more an economical than a metallurgical gain, it is now proved to be a definite metallurgical success; and various refinements that are the natural sequence of a continued operation will no doubt bring the efficiency of the present plant to a much higher state than in any period of the past. Several months after flotation was started, the No. 3 mill, which is a primary unit, was tied into the flotation circuit, operating in water with the washing classifier sands (minus 3⁄16 in. plus 100 mesh) as feed. At first the mill would not run steady in water because of a shortage in settling and cell capacity, but this scheme worked so well that the company was willing to overload the plant, sacrificing a bit on extraction in order to increase tonnage. This sacrifice on extraction, however, was covered by a reduction in costs and this experience has shown that if a new mill were built it should be so designed that primary grinding to a reduction of 48 mesh should be made in water, because the ore seems to be made up of about 55 per cent hard siliceous material and 45 per cent of softer, easily reduced material; and a 48-mesh grind reduced 45 per cent of the total ore to minus 200-mesh; furthermore, on a given heads of $10, the slime portion of the ore at this stage of grinding carries only a value of about $4 per ton and is readily treatable by flotation at a direct flotation cost of from 14¢ to 15¢ per ton. The 55 per cent or harder portion of the ore is proportionately increased in value and treatment is more difficult, but it will yield up its values by fine grinding and cyanidation. With extraction increasing in a fairly definite proportion with relation to the grinding beyond 60 per cent minus 200-mesh (in other words, extraction at 60 per cent minus 200-mesh) is about 91 per cent, while at 90 per cent minus 200-mesh extraction rises to plus 95 per cent. Reduction beyond this stage does not seem practical. Recent ore developments have been of such quantities and grade and in such a location that it seems probable that Benguet may build a new mill in the near future; and for that reason we hesitate to spend any more money on the present mill in order to incorporate this new flow sheet in its entirety.

However, the portion of the old mill that embodies these principles has conclusively proved the value of the scheme, and the new mill undoubtedly will have a flow wherein the ore is washed and reduced to the neighborhood of 48 mesh in water with slime separation in water, the sands continuing on to secondary and possibly tertiary reduction in cyanide; the primary slimes and the slime portion reduced in the primary grinding to be treated by flotation, with the thickened or filtered concentrates joining the sand stream to the secondary mills.

Various experiments are being conducted at the present time, both at the plant and in the United States, to prove or disprove the value of this scheme of treatment, but there is little doubt in my mind that it is the most practical scheme for this particular operation. At least, so far as it has been carried, the practice has solved a perplexing problem of long standing at Benguet, and others faced with a similar slime problem may be able to increase capacity at a low capital cost and at the same time reduce difficulties to a considerable degree.

## DISCUSSION

C. M. Eye, San Francisco, Calif. (written discussion).—Inasmuch as I have had a very considerable part in the development of Benguet milling practice from the earliest days, and am quoted by Mr. Morris, I should like to submit a few comments bearing on the subject so ably treated in this paper.

The fact that the character of the ore handled at different periods has varied greatly is important. At the beginning of operations, all the ore came from above the normal water table and in the main was completely oxidized, at least that portion coming under the category of natural slimes. Gold-bearing sulphides were present in the harder ore and a concentrate was made from the sands product by water concentration on a Wilfley table, which ran over one hundred dollars per ton in gold. If tellurides were present, they were not determined at this stage of the development (from 1906 to 1910).

After operations were resumed in 1915 with the new all-sliming and cyanidation plant, the presence of tellurides in the ore was definitely established. In certain parts of the vein and near the surface occurred bunches of very high-grade ore in which calaverite and sylvanite were easily recognized. Such bunches often assayed over two thousand dollars per ton, and when as sometimes happened, a few cars of this ore was put into the mill, the jump in values all down the line was noticeable. Tailings assays of as much as $4 per ton were occasionally obtained. It was and still is my opinion that such abnormal results were due to the presence of tellurides in the ore. By 1918 the situation had materially improved, and while the tailings were at times rather high in value, these values were not so erratic. By this time the greater portion of the ore milled was coming from the upper portion of the zone of secondary enrichment. It was fairly well oxidized, with amorphous silica as the predominating gangue mineral, and the gold either free or in iron sulphides. Clay and other colloidal materials were not greatly in evidence.

At about this time, a series of exhaustive tests on the ore was made by General Engineering Co., involving treatment by amalgamation, concentration by water or by flotation, and cyanidation, either preceding flotation or applied to final tailings. Their conclusions eliminated amalgamation and water concentration and also flotation, either preceding or following cyanidation, as impractical. It was therefore decided to carry on as before, in spite of the long period of contact necessary and the loss in final tailings attributed to the presence of a small quantity of tellurides. It is my remembrance that the tests confirmed their presence.

In 1921, as noted in the paper, tests were made by the American Cyanamid Co., with conclusions adverse to the introduction of flotation. It is to be noted that in all of these tests, only the application of flotation to the whole ore stream was considered.

During the period under discussion, the main ore supply was coming from the second and third levels of the mine, in the heart of the zone of secondary enrichment, and differed little in character from that in the upper portion of the zone.

In the period from 1921 to 1931 there was a decided change in the composite character of the ore, due to greater depth and to the opening of new ore bodies of rather different character on both extensions of the vein, as well as laterally.

The ore from the deeper mining was harder and contained less free gold and more in iron sulphide, while the ore from the extensions brought in much more colloidal material, and even manganese minerals, never known to occur in the older portion of the mine. This process of change in character in the mill feed has been going on since that time, as shown by the descriptions of ores received by Mr. Morris, and methods of treatment had to be changed accordingly. There is still another change in the character of the ore to the mill due soon, when the large bodies of low-grade calcite in adjoining properties now under process of development are mined. This should introduce no difficult problems however.

I consider that the application of flotation to a colloidal material such as that described, with a concentrate recovery of 85 per cent of its assay value in the form of an easily treated concentrate, and the elimination thereby of a most troublesome factor in cyanidation, is indeed a very notable achievement.

The occurrence of tellurides in the ores of Benguet has, I believe, been definitely established, as has also the fact that these occur in lessening amounts with depth. In the concentrate produced, no tellurides have been identified, as far as I am aware, but a considerable proportion of the gold is free and extremely fine. This gold may have resulted from the decomposition of tellurides in the surface ores or may have come from the decomposition of sulphides. Is it not possible that most of the gold was originally in combination with tellurium and when freed by decomposition migrated to the zone of secondary enrichment to be imprisoned in the crystallization of secondary sulphides?

J. M. Morris.—A new ore body has been developed during the past year (1935) and is now producing up to 15 per cent of the tonnage to the mill. This ore is largely calcite and is of excellent grade. It is a very good cyaniding ore but does not float as well as the regular Benguet ore with which it is mixed in the mine ore passes. This has somewhat disturbed our scheme of flotation; so much so, in fact, that we have had to cut No. 3 mill back to cyanide, and at present we are confining flotation to the primary slimes, which results in a direct flotation recovery of about 86 per cent, or a recovery figured back against a total millheads of 90 per cent.

Recovery on the flotation concentrate runs from 96 to 98 per cent and total mill recovery is at present about 93 per cent, handling at the rate of 800 tons per day.

We are installing a secondary set of filters. When these are put into commission the flow at the tail end of the mill will be: Primary filtration on four 12 by 18-ft. Oliver filters; filter discharge repulped and agitated from 4 to 4½ hr. in a 30 by 20-ft. Dorr agitator; then refiltered on four 12 by 18-ft. Oliver filters. This should result in an increased recovery of about 1 per cent.

# Milling Practice at Demonstration Gold Mines Ltd., Philippine Islands

By George A. Bell,* Member A.I.M.E.

(New York Meeting, February, 1939)

The mine and milling plant of Demonstration Gold Mines, Ltd., is near the city limits of Baguio, Mt. Province, P. I. The mine road connects with the main highway to Manila. The nearest railway point is near sea level, approximately 40 miles distant.

The Baguio district is very mountainous and has one of the heaviest rainfalls in the world. It is therefore difficult to maintain roads or to impound tailings and mine dumps. All supplies are trucked into the district direct from Manila or the nearest railway point, which means uncertain deliveries and high freight rates. Installation of equipment is difficult and costly.

The average elevation at the mine is 4000 ft. and the climatic conditions are ideal except for a three months rainy season.

The company generates its own power for mining and milling operations with three 400-hp. Ruston Diesel engines direct connected to 250-kw. General Electric alternating current generators.

Labor conditions have been excellent, although at present social security laws are causing some unrest. Labor receives a higher average wage rate in this district than other labor in the Islands. The company also furnishes free living quarters, hospitalization and workmen's compensation.

Taxation has been reasonable up to the present time, but some of the new mining legislation may make it difficult to operate and pay dividends. The future depends largely upon the continuation of $35 gold and the political outcome in the Islands.

## History

The Demonstration ore body was worked by the Igorots for many years, as evidenced by old stopes and fill encountered in present operations. Attention of Americans was first attracted soon after the Spanish-American war. During the building of the Benguet road to Baguio, the engineers and foreman became interested in the geology of the district.

---

Manuscript received at the office of the Institute June 27; revised Oct. 25, 1938. Issued as T. P. 1017 in Mining Technology, January, 1939.

* Mill Superintendent, Demonstration Gold Mines, Ltd., Baguio, Mt. Province, Philippine Islands.

In the year 1915, H. P. Whitmarsh and associates took a 99-year lease on claims covering the present location. They operated a small stamp mill and amalgamation plant during 1917–1918, but stopped operations after having milled approximately 10,000 tons of high-grade ore, because of the refractoriness of the ore.

Present development and operations began in 1933, under the supervision of R. L. Lile, who has carried the development work through to the present stage. The operations have returned a substantial profit and Demonstration Gold Mines, Ltd., is one of the few mines in the Islands that have paid dividends from the start. Beginning actual milling operations in the year 1935 with a 100-ton all-slime countercurrent cyanide plant for treating oxidized ores, the plant has been changed and enlarged to treat more than 300 tons per day of refractory sulphide and oxide ores in varying proportions to facilitate mine development. Table 1 gives tonnage and production figures to date.

TABLE 1.—*Tonnage and Production*

| Year | Tons | U. S. Dollars Production |
|---|---|---|
| 1935 | 54,760 | $ 465,176.63 |
| 1936 | 73,985 | 738,172.67 |
| 1937 | 93,562 | 832,002.13 |
| 1938 (8 months) | 72,941 | 663,594.15 |
|  | 295,248 | $2,698,945.58 |

## ORES TREATED

The main ore body occurs as an intrusive formation of andesite and diorite within an older phase of andesite, which caused considerable faulting in the movement. It is composed of sedimentaries, tuffs and diorite phases.

There are two main types of gold ores, oxidized and sulphide. Locally, the ores are classed as manganese-calcite, quartz-calcite and sulphide. There is considerable mixed ore, which is difficult to classify.

The manganese-calcite is a dark brown, clayey ore, which is difficult to handle in chutes and to put through a crushing plant. Difficulties are also caused in thickening and filtering operations. The quartz-calcite is very hard and is sometimes diluted with andesite and other rock. These oxide ores are amenable to cyanidation and except for the contamination with some refractory sulphide will yield a high extraction by straight cyanidation.

The sulphide ore is composed of breccias, andesite and quartz, all extremely hard and tough. This ore is not amenable to cyanidation or amalgamation under ordinary conditions. The refractory nature of the sulphide ore is due to highly coated gold particles and their association with copper, lead, zinc and other sulphides. The gold is released from the sulphides at ordinary grinding, except for a small percentage locked with the chalcopyrite, galena and quartz.

Extensive research on the nature of the gold coatings definitely showed them to be mainly bismuth, although copper, iron and slime coatings were also in evidence. The color ranges through black, brown and green and the particle size from 65 mesh down to the colloidal state. Treatment with strong acids or dilute solutions of mercuric salts will remove the coatings and render the gold soluble in cyanide solutions or amenable to amalgamation.

The sulphide ore is composed mainly of: sphalerite (two forms), galena, pyrite, pyrrhotite, chalcopyrite, bornite, chalcocite, covellite. The carbonates and oxides of copper, zinc, iron, lead, and arsenic are all present in the ore as well as water-soluble forms of copper and iron.

The sulphide minerals are intergrown to a considerable extent and blebs of minerals occur entirely within other mineral particles. Extremely fine grinding would be required for selective flotation, as this condition is clearly shown even in the minus 325-mesh particles. Chalcopyrite and galena are sometimes hosts for the gold, but the greater part of the gold is released at ordinary grinding.

Pyrite and sphalerite have been shown by microchemical tests to be comparatively free of gold. The pyrite is easily depressed in the flotation operations without serious gold losses. The free sphalerite, however, is strongly activated by the presence of considerable soluble copper and is difficult to depress. Excessive cyanide or other depressants are required as well as close control of the quantities of collectors. The blebs or intergrowths of sphalerite with copper minerals and galena constitute the most serious problem.

The sulphide ores are not amenable to cyanidation or amalgamation under ordinary conditions, for the reasons stated. A large amount of test work has been done on all practical means of gold recovery as well as on the base metals present in the ores. The outstanding results obtained were by the use of mercuric salts and acids (as mentioned above) in obtaining a high extraction of the refractory gold by cyanidation. However, because of the equipment necessary for cyanide regeneration and high reagent costs, this scheme was not quite as practical under the present conditions as the present method of treatment.

## Present Treatment

The present milling plant consists of two sections with a combined daily capacity of 300 to 400 tons. The cyanide section for oxide ores has a maximum daily capacity of 250 tons and the flotation section for refractory sulphide ores has a maximum daily capacity of 150 tons. The flotation section began operation Sept. 20, 1937. These tonnages may be varied considerably by simple alterations to facilitate the mining program.

Fig. 1 is a general metallurgical flowsheet of treatment, showing principal equipment with metallurgical data and analysis. All ore

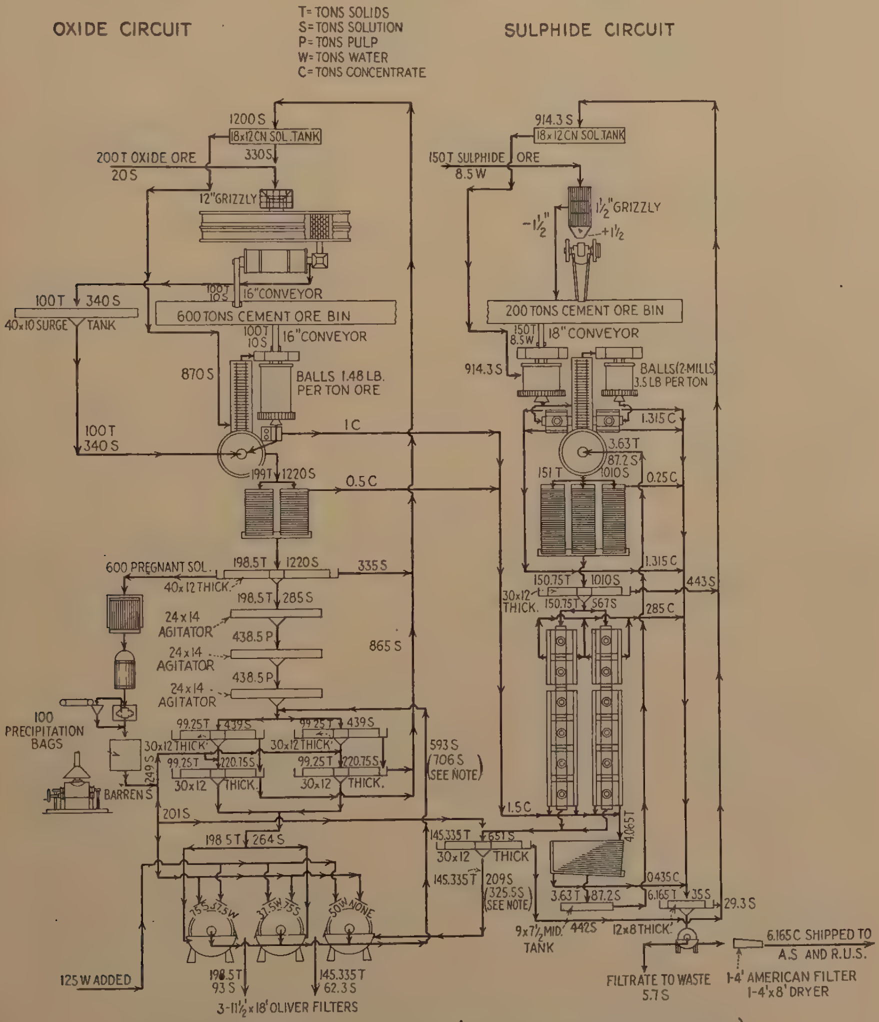


FIG. 1.—GENERAL FLOWSHEET (DETAILS ON OPPOSITE PAGE).

is delivered to the mill in 20-cu. ft. tram cars. The ores are crushed in separate crushing units. Because of the high moisture and clayey nature of the oxidized ore, a washing plant is necessary before the ore can be reduced to a suitable ball-mill feed. This has been accomplished by the installation of the Hadsel mill as a combination washing and crushing unit. The sulphide ore is easily handled over a grizzly and jaw crusher. Increased tonnage may be obtained by the installation of secondary fine crushers.

The main feature, as shown in the general flowsheet, is the interlocking of the two circuits. A small amount of refractory sulphides and coated gold is recovered from the oxide circuit by the use of mineral jigs and corduroy tables and the concentrate is transferred to the sulphide

---

### FIG. 1.—GENERAL FLOWSHEET.

#### *Oxide Circuit*

*Chemical Analysis of Ore:* Au, 0.28 oz. per ton; Ag, 0.40 oz. per ton; $SiO_2$, 58.5 per cent; Cu total, 0.15; Cu oxide, 0.02; Pb, 0.25; Zn, 0.80; Fe, 4.20; S, 0.75; $Al_2O_3$, 6.50; CaO, 13.40; $MnO_2$, 0.60; As, 0.01; Sb, tr.

*Washing Plant:* 20 by 4-ft. Hardinge Hadsel mill. Interior grizzly openings 1⅝ in. Discharge to 3 by 8-ft. Hardinge Hadsel countercurrent classifier.

*Grinding and Classification:* 5 by 8½-ft. ball mill in closed circuit with 200-ton Denver jig and 26 by 4-ft. Dorr classifier with 9-ft. diameter bowl overflowing 60 per cent minus 200.

*Tables:* two 5 by 12-ft. corduroy tilting tables.

*Precipitation:* 600-ton Merrill-Crowe precipitation plant.

*Refinery:* type 92S double-burner Monarch bullion furnace and dust chamber.

*Bulk Flux:* minus 10-mesh silica, 32 per cent; borax glass, 30; soda ash, 20; hematite, 10; manganese dioxide, 8.

*Bullion Analysis:* Au, 48.30 per cent; Ag, 22.03; Pb, 8.28; Cu, 19.61; Zn, 1.08; Fe, 0.40; S, 0.04; undetermined, 0.26.

#### *Sulphide Circuit*

*Chemical Analysis of Ore:* Au, 0.354 oz. per ton; Ag, 0.590 oz. per ton; $SiO_2$, 65 per cent; Cu total, 0.70; Cu oxide, 0.05; Pb, 0.60; Zn, 2.20; Fe, 6.55; S, 2.20; $Al_2O_3$, 7.70; CaO, 2.20; $MnO_2$, 0.50; As, 0.02; Sb, tr.

*Crushing Plant:* 10 by 16-in. type H Traylor jaw crusher set at 1½ inch.

*Grinding and Classification:* primary grinding unit, 7 by 5-ft. Traylor ball mill discharge oversize to 26 by 4-ft. Dorr classifier with 9-ft. diameter bowl. Fines to 36-in. Fagergren flotation cell. Tail to classifier. Secondary grinding unit, 5 by 4-ft. A.C. ball mill in closed circuit with 36-in. Fagergren flotation cell and classifier named above. Overflow 60 per cent minus 200.

*Tables:* three 3 by 19-ft. corduroy tilting tables.

*Flotation:* twelve 36-in. Fagergren flotation cells and one No. 6 Wilfley table.

*Concentrate Analysis:* Au, 7.691 oz. per ton; Ag, 7.000 oz. per ton; $SiO_2$, 18.970 per cent; $Al_2O_3$, 2.920; Fe, 12.300; CaO, 1.220; Cu, 12.250; Zn, 12.500; S, 18.300; Pb, 12.120.

#### *Reagents*

*Chemical Agents Consumed:* NaCN, 1.51 lb. per ton ore; CaO, 15.9; Zn dust, 0.10; PbAc, none.

*Flotation Reagents Consumed:* Na xanthate Z4, 0.09 lb. per ton ore; pine oil, 0.05; CaO, 6.00; NaCN, 1.00.

### SCREEN ANALYSIS OF TAILINGS

| Oxide Tailings | | Size | Sulphide Tailings | |
|---|---|---|---|---|
| Per Cent by Weight | Assay, Oz. Au per Ton | | Per Cent by Weight | Assay, Oz. Au per Ton |
| 14.00 | 0.031 | +100 | 10.00 | 0.04 |
| 11.00 | 0.036 | +150 | 12.00 | 0.040 |
| 15.00 | 0.031 | +200 | 16.00 | 0.040 |
| 60.00 | 0.020 | −200 | 62.00 | 0.030 |

circuit. Any soluble gold in the oxidized slime present in the sulphide circuit is dissolved by the cyanide used to depress sphalerite. The soluble values are recovered by filtration and added to the cyanide circuit. The dilution is balanced by an equal discard of barren solution to the sulphide circuit for grinding solution. Another feature is the use of unit cells and corduroy tables to recover most of the free gold before flotation. Since this gold will not amalgamate or cyanide under ordinary conditions, it is added to the final concentrate, which is shipped to the Tacoma smelter.

Because of the high freight and treatment charges, fine-grinding expense, etc., as well as low metal prices, selective flotation has not been practiced.

TABLE 2.—*Operating Results Cyanide Section*, 1937

| Tons Milled | Au Assay, Oz. per Ton | Tailings, Ounces Au per Ton | | | Extraction, Per Cent | Consumption | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Lb. per Ton | | | | Kw-hr. per Ton |
| | | Solution Loss | Insoluble | Total | | NaCN 100 Per Cent | CaO 70 Per Cent | Zinc | Balls | |
| 82,839 | 0.282 | 0.006 | 0.027 | 0.033 | 88.3 | 1.37 | 13.6 | 0.09 | 1.48 | 23.0 |

TABLE 3.—*Direct Milling Costs Cyanide Section*, 1937
(U. S. DOLLARS PER TON)

| Operation | Per Ton | Operation | Per Ton |
|---|---|---|---|
| Washing and crushing........... | $0.1240 | Refining and marketing bullion. | $0.1765 |
| Grinding and classifying......... | 0.2835 | Assaying..................... | 0.0320 |
| Thickening and agitating........ | 0.0595 | Supervision.................. | 0.1665 |
| Solution handling (includes reagents)...................... | 0.3625 | Tailing disposal and miscellaneous.................. | 0.0435 |
| Filtering....................... | 0.1030 | | |
| Clarification and precipitation.... | 0.0690 | Total direct cost per ton..... | $1.4160 |

TABLE 4.—*Operating Results Flotation Section*, 1938
(8 MONTHS)

| Tons Milled | Ounces Au | | | Gold Extraction, Per Cent | Ratio of Concentration | Consumption | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Lb. per Ton | | | | | Kw-hr. per Ton |
| | Heads | Tails | Concentrate | | | NaCN | CaO | Z-4 | Pine Oil | Balls | |
| 32,739 | 0.354 | 0.035 | 7.691 | 90.53 | 24.0 | 1.00 | 6.00 | 0.09 | 0.05 | 3.50 | 26.0 |

Table 2 gives operating results of the cyanide section for the year 1937. Table 3 gives direct milling costs of the cyanide section for the year 1937 and Table 4 operating results of the flotation section for eight months of year 1938. Table 5 gives an analysis of the metals present in the ore, concentrates and tailing, and Table 6 gives the direct operating costs per ton for the flotation section.

TABLE 5.—*Flotation Section Analysis,* 1938
(8 MONTHS)

| | Per Cent Weight | Ounces per Ton | | Per Cent | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Au | Ag | Cu | Pb | Zn | Fe | S |
| Heads | 100.00 | 0.354 | 0.59 | 0.70 | 0.60 | 2.20 | 8.70 | 2.20 |
| Concentrates | 4.16 | 7.691 | 7.00 | 12.25 | 12.12 | 12.50 | 12.30 | 18.30 |
| Tails | 95.84 | 0.035 | 0.31 | 0.20 | 0.10 | 1.75 | 8.11 | 1.5 |
| Extraction, per cent | | 90.53 | 49.36 | 72.8 | 84.0 | 23.7 | 6.0 | 34.6 |

TABLE 6.—*Direct Milling and Marketing Costs Flotation Section*

| | Per Ton | U. S. Dollars per Ton | | Per Ton | U. S. Dollars per Ton |
|---|---|---|---|---|---|
| Operation: | | | Marketing expense: | | |
| Crushing | $0.0400 | | Freight, etc., on concentrate | $1.0722 | |
| Fine grinding | 0.4325 | | | | |
| Flotation | 0.3735 | | Smelter charges, deductions and credits | 0.4480 | |
| Concentrate handling | 0.1415 | | | | |
| Supervision | 0.1265 | | | | |
| Assaying | 0.0430 | | Total marketing expense | | $1.5202 |
| Miscellaneous | 0.0710 | | | | |
| Total direct cost per ton | | $1.1900 | Total milling and marketing expense | | $2.7102 |

# The Achotla Chloridizing Mill

By H. P. Allen,* Member A.I.M.E.

(New York Meeting, February, 1937)

The Achotla mill of the Cia. Minera de Peñoles is of special interest in that it is one of the few still employing the chloridization process. The ore milled comes from the Suriana mine and consists of both oxide and sulphide, from neither of which can the gold or silver be extracted by a simple cyanide treatment. The mill was built in 1927, after several years of study in the development of the process[1], and operated from December of that year until October 1930. Operations were resumed in February 1935, and have been continuous since, treating approximately 5000 tons per month, while the mine is getting up to full tonnage of 6500 tons per month.

## TRANSPORTATION OF SUPPLIES

The property is in Guerrero, Mexico, some 175 km. by airline southwest of Mexico City. The mill site is at Temisco (Fig. 1), 8 km. from the Balsas River and 4.8 km. by aerial tram from the mine. At Temisco are the general office, shops, warehouses and laboratory serving both mine and mill. Here sufficient water is available either from a small creek running through the property or from the Balsas River, also convenient and ample storage space for the tailings.

With the exception of the mine timber and a few native building materials which may be obtained locally, all supplies for both mine and mill are brought down the Balsas River from Balsas, the terminal of a Mexican National Railway line out of Mexico City. The method of transportation on the river is interesting. Rapids with very fast water are numerous, prohibiting the use of mechanically propelled boats. Those used resemble large, flat-bottomed rowboats some 22 ft. long by 8 ft. wide (Fig. 2). They are manned by two oarsmen sitting in the bow, each handling one large oar, and usually another man in the stern who, with his oar, assists in steering the boat, especially when the rapids are run. From 3 to 7 tons of freight are carried on each boat, depending upon the stage of the water, which governs also the time

---

Manuscript received at the office of the Institute Oct. 19, 1936. Issued as T.P. 773 in Mining Technology, January, 1937.

* Mill Director, Achotla Unit, Cia. Minera de Peñoles, S. A. (subsidiary The American Metal Company, Ltd.), Temisco, Gro., Mexico.

[1] References are at the end of the paper.

required to make the 85-km. trip. This varies from 7 hr. when the water is high to 16 hr. toward the close of the dry season, when it is low. While going down the river does not require great energy, the return trip upstream is different for then the boats must be pulled by hand, which requires four or more men. Even so, up to 500 kg. of outgoing freight per boat are accepted.

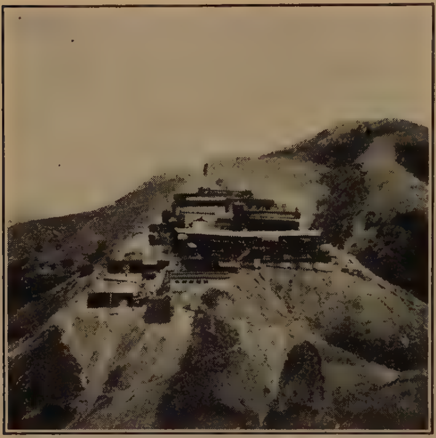


Fig. 1.—The Achotla mill.

From the river to the mill, transportation of the freight is over a 36-in. gauge track but here the motive power is furnished by teams of bulls (Fig. 3). By means of a yoke over the horns, each team is hitched to a small flat car. The cargo is up to 3 tons. Materials for the mine, including a large portion of the mine timber, are transported to the cable station at the top of the mill by means of an incline tram, which serves the mill also. From the mill to the mine, an aerial tram is the final link in the transportation system.

## The Process

The mill utilizes the Holt-Dern process of chloridization as originally applied to silver ores in the Park City and Tintic districts of Utah[2]. Essentially this comprises preparing the ore for leaching by blast-roasting a mixture of oxide ore, sulphide ore and salt, without other fuel than the sulphide ore. The leaching, however, is by percolation with cyanide after a preliminary water and acid wash rather than with brine, this being necessary on account of the presence of gold. The flowsheet is shown in Fig. 4.

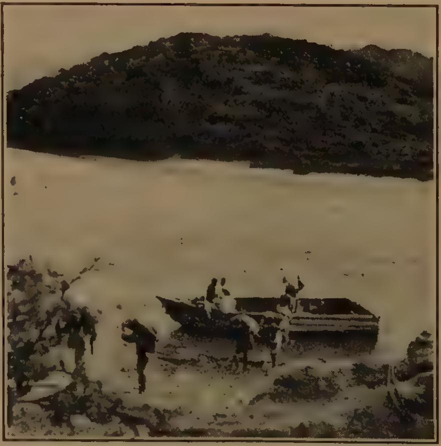


Fig. 2.—A Balsas River boat.

## Grinding

The ore is crushed at the mine to 2½ in. and conveyed to the mill by aerial tram. It is received at the top of the mill in three 175-ton steel bins, one of which is reserved for sulphide, the other two for oxide.

By belt conveyors it may be delivered from these to two wood-fired Ruggles-Coles, class A-8 driers or to two steel surge bins ahead of the crushing plant. Since crushing is "dry," it is necessary that the moisture content be not over 7 per cent, hence the driers are used from June to the latter part of December.

All grinding, including the grinding of the salt, is done with rolls. For the first reduction of the ore from 2½ to ⅝ in., one set of Allis-Chalmers 48 by 16-in. rolls in closed circuit with a No. V.32, 4 by 5-ft. Hum-mer screen is used. The undersize passes to two sets of Allis-Chalmers 36 by 16-in. Superior rolls working in parallel, each in closed circuit with two 4 by 5-ft. Hum-mer screens. When the oxide ore is being ground these screens are equipped with Tyler Ton-Cap cloth, with a clear opening of 0.125 in.; when sulphide ore or salt is being ground the screens are equipped with Tyler Ton-Cap cloth with a clear opening of 0.09 in. The salt is fed directly to the 36-in. rolls by belt conveyor from concrete storage bins having a capacity of 1200 tons. It is not highly hydroscopic and so can be ground with the rolls without previous drying or mixing with the ore, as is necessary with some commercial salts. Its moisture content will go up to 5 per cent during the rainy season and at such times there is some blinding of the screens, but this is not serious.

Fig. 3.—Hauling salt.

None of the grinding offers any particular difficulty or involves any unusual features. The oxide is soft and easily ground. The sulphide is very hard and unless the primary crushers at the mine are kept well set up, the larger pieces will ride the 48-in. rolls and corrugate them. Even so the shells can be used until worn to less than an inch thick.

The final product from the rolls falls onto a 16-in. belt conveyor passing over a Merrick weightometer and delivering through an automatic sampler to a shuttle belt. By means of the latter the oxide is run into any one of four 200-ton steel bins as desired, the sulphide into one of two 200-ton steel bins and the salt into a wooden bin holding 150 tons. Each bin of ore is designated a "mill lot," given a number and analyzed.

## Mixing Plant

For purpose of control the oxide-mill lot to be mixed is analyzed for sulphide sulphur and tested with a small blast roaster to determine the

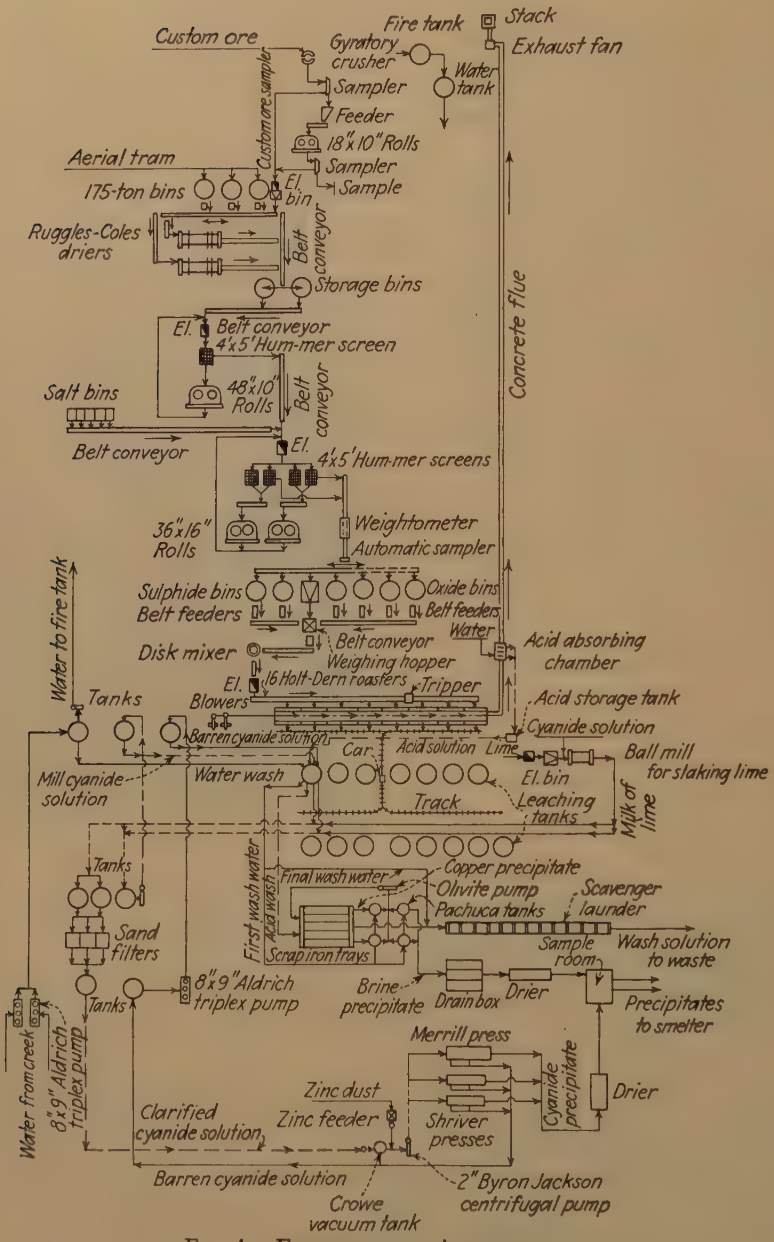


FIG. 4.—FLOWSHEET OF ACHOTLA MILL.

chlorine loss. The sulphide ore is analyzed daily for sulphide sulphur and the salt for chlorine. With this information a blast-roaster charge, consisting of oxide ore, sulphide ore and salt, is calculated. It was discovered during the first period of operation of the mill that a certain more or less definite minimum amount of chlorine must be left in the calcines from the roasters in order to obtain acceptable chloridization. This is approximately 3.3 per cent. If it falls under this amount, the chloridization of the values usually diminishes rapidly, while more appears to be of small benefit. In calculating a roaster charge allowance is made for this as well as for the chlorine that is volatilized. To obtain the desired temperature in the roast, the sulphide sulphur content of the charge will run about 4.5 per cent, varying with the rate of burning, which depends upon the porosity of the charge and the blast pressure being used. To mix the three ingredients, 400 kg. of oxide is first run by conveyor belts from the mill lot bin to a weighing hopper equipped with a Howe dial scale having an accuracy of 2 kg. Next, the proper amount of sulphide, 100 kg. more or less, is run into the weighing hopper in the same manner, then the salt, around 90 kg., and finally another 400 kg. of oxide. The batch having been thus weighed out, a gate in the bottom of the weighing hopper is gradually opened, allowing the content to fall to a conveyor belt. It is discharged into an 8-ton cone-shaped hopper over a 7-ft. disk mixer. The disk or plate mixer is of the type that is frequently used for mixing and feeding the Dwight-Lloyd roaster charge in lead smelters. While the mixing with this is not quite as good as that obtained with a revolving drum or concrete mixer, it is satisfactory for the purpose, avoids the necessity of frequent cleaning when the mix is a little damp and requires no attendant. The charge from the mixer goes to a bucket elevator delivering to a tripper belt for distribution over the bins of the Holt-Dern roasters.

A certain amount of agglomeration of the ore particles of the charge is essential for its proper burning in the blast roasters. Since the charge usually contains between 6 and 7 per cent water, this agglomeration is attained in the mixing and handling. If additional moisture is necessary, brine solution from the leaching plant is sprayed onto the charge as it is discharged from the buckets of the elevator.

## Roasting

There are 16 Holt-Dern blast roasters in two rows of 8 each. They are the standard type with a roasting chamber 5 ft. 8 in. by 10 ft. 6 in. by 30 in deep. The reciprocating motion of the grates is transmitted from line shafts through 15-in. Dodge friction clutches, two clutches for each roaster in order that motion may be imparted to the grates in each half of the roaster independently. Air blast is supplied by an American Blower, No. 14 type P, having a capacity of 25,000 cu. ft. per min. at

965 r.p.m. at 8 oz. per sq. in. discharge pressure. In practice the pressure is varied from 4 to 10 oz. as desired, by adjustment of a damper. The blower is belt-connected to a 100-hp. synchronous motor. A spare blower with motor is provided. The roaster smoke is drawn through a concrete flue by an American Blower Corporation fan, size 12, series 13, the impeller and shaft of which are covered with rubber, and is discharged through a 30-ft. wooden stack located well up the slope above the mill. The calcines, after they are shaken through the grates of the roasters, pass down a chute from the roaster hoppers to a concrete bin running the whole length of the roaster block, and from this bin they are trammed by hand to the leaching tanks.

The roasters are started the first time by covering the grates with 8 or 10 in. of finely split wood over which is sprinkled a little fuel oil to assure even ignition. The wood is allowed to burn until only glowing coals remain, then the ore charge is run on from the bins above, leveled even with the working doors and tamped a little around the walls, after which the air blast is allowed to enter beneath the grates. The sulphide ore in the charge burns gradually upwards, and its oxidation, and other exothermic reactions that take place in this kind of a roast, bring the temperature of the whole charge up to approximately 650° C., sustaining it at this maximum point for perhaps 15 min. When the charge has burned to the top, the air blast is cut off, the grates set in motion and the calcines shaken down until only about 12 in. remain. This is broken up, leveled, another batch of ore charge run on and the operation repeated, the hot calcines that are allowed to remain on the grates serving to ignite the fresh charge so that no rekindling is necessary. With a blast pressure of 7.5 oz., a roaster will burn through in from 3 to 4 hr., depending on the permeability of the charge to the air. It requires 20 to 30 min. to shake it down and recharge. The amount of ore roasted per charge varies with its weight per unit volume. With Suriana ore this averages 2¾ tons, equivalent to 16½ tons of dry ore per roaster day.

The Holt-Dern roaster has many advantages. No fuel other than the sulphide ore is required, volatilization and dust loss are low, making it unnecessary to install dust-collecting equipment. Exclusive of the cost of salt, operation and maintenance cost is reasonable considering the small scale of operation. At Achotla this cost, plus the cost of mixing the charge, has amounted to 38¢ U. S. Cy. per metric ton of dry ore treated. It does not require a great deal of skill to operate the roaster, although reliance must be placed in the furnacemen, as they must break up and level properly the hot bed of calcines before adding each new charge. The salt, of course, must be added at the beginning of the roast. With certain classes of Suriana ores, this is a disadvantage. Foot-wall rock and portions of the ore gangue near the foot wall act decomposingly on salt and, while the chlorine product resulting from this reaction is largely hydrochloric acid, it is expelled, apparently, before some of the silver minerals are in a condition to be chloridized. Hence, in order to obtain satisfactory chloridization when the ore contains this type of gangue, it is necessary to add enough salt to the roaster charge to satisfy the gangue in addition to that required normally. If, on the other hand, the ore could be heated before the addition of the salt, chloridization would be effected without an excessive, premature salt decomposition, resulting in a saving of from 2 to 4 per cent. Even so, any chloridizing furnace demanding the use of fuel other than sulphide ore would be of doubtful economic advantage in this district on account of the high cost of all fuels.

The gangue material that decomposes the salt is classified by the petrographer as a "carbonated sericite schist." It contains quartz plus sericite, 50 per cent; carbonate, hematite and limonite, 45 per cent and small amounts of apatite, leucoxene and pyrite. The sericite, a type of muscovite mica, appears to be the particular mineral that reacts with the salt. Additional microscopic work is in progress to obtain more information as to just what the chemical reaction is.

With salt costing, delivered, $18.25 U.S.Cy. per metric ton, the matter of economy in its use is ever one of concern. Reliance is placed on careful mining to avoid contamination of the ore by the salt-consuming gangue and by repeated testing of the ore before roasting to determine the exact amount of salt to be used. At one time a portion of the sodium chloride was recovered from the leaching-plant wash liquors. This required, first, a recirculation of these liquors through the calcines in order to increase the sodium chloride concentration. The process then involved the removal of sodium sulphate by "freezing" and crystallization, after which the brine was sprayed over a bed of coarse ore through which was blown air heated by drawing it through pipes in the roaster calcine bins. The salt was deposited on the coarse ore and this was periodically reclaimed and treated in the regular manner, its salt content reducing the new salt requirement an equivalent amount. The process is not used at present. The necessity for supplementing the heat obtained from the calcines, the deposition of zinc chloride from the brine liquors along with the sodium chloride, and the increased amount of metals dissolved by the brine in its recirculation through the calcines, were factors that gave preference to the present procedure. The equipment is intact and may be used if conditions in the salt market make it feasible.

## Leaching

All leaching is by percolation, no slime separation being necessary. The practice is to remove the soluble salts and cyanicides by washing and then to extract the gold and silver with cyanide. The calcines from the roasters are drawn into side-dump cars holding one ton and trammed by hand to redwood leaching tanks. Of these, fourteen are 30-ft. dia. by 8-ft. staves and one is 35-ft. dia. by 7-ft. 6-in. staves. They hold 180 and 210 tons respectively. The filter consists of the usual false bottom of wooden strips over which is stretched one thickness of "Lechuguilla," or cocoa matting. No duck or burlap is used. The matting has a life, prolonged by a little patching around the discharge gates, of 6 months. Each tank has two 12-in. bottom-discharge gates, made of hard lead to withstand the corrosive action of the brine with its dissolved salts. The 4-in. effluent pipe is of hard lead also, a rubber hose on the end with a pinchcock serving to direct the solutions to the proper launders and to adjust the flow.

The calcines as they come from the roaster bins are hot and, to avoid injury to the tank and filter, just enough water is run into the tank to protect them. When filling is completed, the cone-shaped pile of calcines, formed when the cars are dumped, is roughly leveled with a stream of water and then by hand. The tanks are filled to within 6 to 18 in. of the top, depending on the tonnage being handled. After leveling, the tank is completely filled with water, then the pinchcock on the effluent pipe is opened and the tank drained to storage for subsequent precipitation of the gold and silver. The tank is next filled with a weak solution of acid, which is obtained by spraying water into an absorbing chamber in the roaster flue. The acid is a mixture of hydrochloric and sulphuric and the solution contains about 5 grams per liter in terms of HCl. The tank having been filled with this, the effluent line is opened again and the solution directed over shallow concrete trays holding scrap iron, and from these flows to waste through 150 ft. of "scavenger launder," filled with tinplate cuttings. The weak acid wash is continued for 4 hr., then water is substituted for the acid and washing is continued until the effluent shows no reaction for acid with methyl orange, and zero gravity. The tank is then drained, filled with water and again drained, after which cyanide leaching is started. The wash solutions, by virtue of their sodium chloride content, dissolve 37 per cent of the total silver that is extracted. They dissolve gold to the extent of 27 per cent of the total extracted, probably by virtue of its conversion to a chloride after the calcines are drawn from the roasters.

The cyanide solutions contain 1 kg. per metric ton KCN and have an alkalinity of from 0.300 to 0.700 kg. per ton CaO as they are pumped to the leaching tanks. After passing through the calcines the alkalinity drops to zero. Only occasionally, at the end of the cyanide leach, will the cyanide effluents be even slightly alkaline. Milk of lime is run into the launders receiving the leaching-tank effluents. This is prepared by slaking burned lime with barren cyanide solution in a ball mill, the resulting lime suspension passing directly from the ball mill to the launders. There are three cyanide solutions designated "pregnant," "mill" and "barren," distinguished principally by their gold and silver content although the alkalinity of the mill solution is maintained a little higher than the others.

Percolation rate of all solutions is rapid, diminishing from 14 in. per hour at the start to 6 in. at the end of the leach. This rate can be maintained if the filters are taken up every three months for removal of the slimes that have passed through them.

A representative leaching schedule is as follows:

| | Hours |
|---|---|
| Filling tank with calcines, leveling and filling with water | 24 |
| Draining to brine storage | 3 |
| Filling with weak acid solution | 1 |
| Acid wash to iron trays | 4 |
| Water wash to iron trays | 4 |
| Water wash to scavenger launder | 40 |
| Draining to scavenger launder | 3 |
| Filling with water | 1 |
| Draining to scavenger launder | 5 |
| Filling with mill cyanide solution | 2 |
| Mill solution to mill-solution storage | 2 |
| Mill solution to pregnant storage | 24 |
| Mill solution to mill storage | 120 |
| Barren solution to mill storage | 24 |
| Water wash to mill storage | 2 |
| Draining to mill storage | 5 |
| Discharging tails | 7 |
| Total time | 271 |

Boxes for scrap iron and tanks handling the wash liquors are made of concrete. All cyanide-solution storage tanks are steel, 30-ft. dia. by 20 ft. deep. There is one to receive the mill-solution effluents, two for the pregnant effluents and a mill and a barren tank above the level of the leaching tanks. Mill solution containing the lime sludge is pumped with 4-in. Wilfley pumps, barren solution with an 8 by 9-in. Aldrich triplex. Piping is so arranged that the mill solution may be pumped from the lower tanks directly to the leaching tanks or to the upper storage, from which it flows by gravity to the leaching tanks.

The tanks are discharged by flushing the tails through the two bottom gates, with a fire hose. They flow by gravity to the tailing pond. Approximately 1.4 tons of water per ton of tailings is used for this purpose.

## PRECIPITATION

The values in the wash liquors are precipitated on scrap iron. Copper and a little lead come down with the gold and silver and there is more or less deposition of basic salts of iron and alumina, so that the product is relatively low grade. It has averaged 1.339 kg. Au and 93.700 kg. Ag per metric ton, 30.3 per cent Cu, 13.7 per cent Pb and 1.9 per cent Zn. It is possible to raise the grade of a portion of this somewhat by agitating the first 60 tons of solution coming from the leaching tank with the precipitate that is deposited on the scrap iron, the copper which this material contains acting as the precipitant for the gold and silver. This is done in Pachuca tanks, of which there are four, the solution so treated being worked up in batches. The resulting product contains 2.5 kg. Au, 250 kg. Ag, 8 per cent Cu, 8 per cent Pb and 1.5 per cent Zn. The brine precipitates are washed by agitation and decantation, drained in a concrete box having a canvas filter in the bottom, and dried on iron plates over a wood fire, after which they are sampled and sacked for shipment.

The pregnant cyanide solution, which carries in suspension a considerable amount of lime sludge, since milk of lime is run into the effluent launders from the leaching tanks, is agitated both with air and by means of a centrifugal pump. Care is taken that the alkalinity is very close to 0.300 kg. CaO per ton, this being attained by adding either more lime or more solution to the batch being treated. After agitation, the solids are allowed to settle and the clear liquor drawn off to a sand filter. If the alkalinity goes much over 0.300 kg. CaO per ton, or if agitation has been insufficient, calcium sulphate crystals form in the filter bed and check the filtration, and may continue to form even in the zinc press. Working as indicated, this difficulty is avoided. The sand filter is a concrete box 16 by 49 by 5 ft. deep inside, divided into three compartments each with an area 16 by 16 ft. These have a false bottom of wooden slats over which is stretched a layer of cocoa matting and on this tailings are spread to a depth of 8 in. Two of these sections furnish ample filtering area, so there is always one section in reserve. Once a week the top 3 or 4 in. of tailings are removed, the remainder turned over and an additional quantity added and leveled to the original depth. For 15 or 20 min. after a newly prepared filter goes into use, the filtrate is not entirely clear, so this is returned to the filter with a centrifugal pump. Subsequent filtrates are crystal clear and flow by gravity to a 30 ft. dia. by 20-ft. steel tank from which they are drawn for precipitation.

At present precipitation is with zinc dust but without previous removal of the air from the solution, the Merrill-Crowe vacuum system being temporarily out of order. A 2½-in. single-stage Byron-Jackson centrifugal pump delivers the clarified solution to a 52-in., 32-frame Merrill press and the zinc is fed on the inlet side. Working in this manner, 1.1 units of zinc dust per unit of gold plus silver precipitated is required. Of the combined values silver constitutes by weight 97.8 per cent. The Merrill press is opened for cleaning on the twenty-fifth of each month, the solution being turned into two 24 by 24-in. Shriver presses for the remainder of the month and returned to the Merrill press on the first. The precipitate is dried in iron pans over a wood fire, sampled and sacked for shipment. Fifty kilos are packed in a double canvas sack, over which is drawn one of heavy burlap. All precipitates are shipped by boat to Balsas and thence by train to the company's refinery at Monterrey. The cyanide precipitate has averaged 15.8926 kg. Au, 694.219 kg. Ag per metric ton, 3.4 per cent Cu, 3.8 per cent Pb, 5.9 per cent Zn.

The average analysis of the ores treated, the calcines or leaching-tank heads, and tails for the present campaign are shown in Table 1. The weight of the tails is approximately 90 per cent of the weight of the calcines.

TABLE 1.—*Analyses of Ores, Calcines and Tails*

| | Grams per Metric Ton | | Per Cent | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Au | Ag | Pb | Cu | Zn | $SiO_2$ | Fe | S |
| Oxide ore | 7.87 | 398 | 3.0 | 0.1 | 0.9 | 60.0 | 12.5 | 1.0 |
| Sulphide ore | 4.76 | 468 | 1.7 | 0.6 | 5.6 | 11.5 | 29.8 | 37.5 |
| Calcines | 7.26 | 390 | | | | | | |
| Tails | 0.76 | 71 | | | | | | |

The indicated extraction as calculated from the tank heads and tails has been 90.6 per cent Au and 83.6 per cent Ag. The actual recovery has been approximately 3 per cent lower in both gold and silver. The ore varies considerably in its amenability to the process, that entirely free from the foot-wall gangue permitting an extraction of 93 per cent of the gold and 92 per cent of the silver.

Reagent consumption has averaged 112 kg. of salt, 10.6 kg. of lime, and 1.0 kg. of cyanide per metric ton of dry ore treated. The salt, which is shipped from Isla del Carmen in the Golfo de California, contains, after drying, 53.3 per cent Cl equivalent to 88 per cent NaCl, 0.45 per cent $SiO_2$, 0.03 per cent Fe, 3.68 per cent CaO, 0.34 per cent MgO, 0.01 per cent $Al_2O_3$. The moisture content varies from 2.5 to 5 per cent. The burned lime contains 80 per cent available CaO. Power consumption amounts to 29 kw-hr. per metric ton of dry ore treated.

## MILL CREW

The mill work is directed by a general foreman, three shift bosses and a supervisor in charge of maintenance and construction, all foreigners. The operators are natives, 250 shifts or man-days per 24 hr. being required, which is equivalent to 1.5 men per ton of dry ore treated.

## CUSTOM ORE

The mill accepts for treatment limited quantities of ore from the small mines in the district. This amounts to about 15 tons per day and is, relatively, of high grade, running from 30 to 75 grams Au and 800 to 1500 grams Ag per metric ton. Some of it is so fine that it can be treated successfully in the Holt-Dern roasters only by mixing it with the regular mine shipments. It is all delivered in sacks by burro trains, at the top of the mill, where it is weighed and passed through a small sample mill consisting of a gyratory crusher set to 1 in. and a set of 18 by 10-in. rolls, which grind to ¼ in. A Snyder sampler cuts out one-tenth from the crusher discharge, diverting it to a feeder over the rolls, and a second Snyder sampler cuts out one-tenth from the roll discharge, which constitutes the sample sent to the laboratory for final preparation and assay. From none of the custom ore received can the metals be extracted by a simple cyanide treatment.

## Other Preliminary Treatments Tested

In general, the ores of the district offer an intensely interesting subject for research looking to the development of a process more economical than the salt roast. The gold in Suriana oxides can usually be rendered soluble by some kind of a preliminary acid treatment. Acid brine, or a solution of sulphur dioxide as applied to certain manganese-silver ores, helps in dissolving gold, and the solubility of the silver also is increased, although not even a trace of manganese can be found in most of the shipments. This suggests that the gold and perhaps even some of the silver minerals are coated with a substance impermeable and insoluble in cyanide, in a manner similar to the gold in samples of tailings studied and described by Dr. R. E. Head[4]. On the other hand, a few small streaks of manganese can be detected in the mine and the silver associated with it is rendered soluble to a considerable extent by a sulphur dioxide treatment, so that possibly manganese is responsible for the insolubility of some of the silver even though it is not detected ordinarily in the regular shipments. A reducing roast helps the silver extraction a little. A low-temperature oxidizing roast, as suggested by the U. S. Bureau of Mines[5], aids in silver extraction if the temperature does not exceed 400° C. This procedure in the work cited was applied to silver minerals containing arsenic and antimony. The silver in silver jarosite also appears to be rendered soluble in cyanide by an oxidizing roast at 400° C. A sample of this mineral containing 18.5 per cent silver obtained from the Tintic Standard Mining Co., where it was first identified[6], gave up nearly 100 per cent of its silver to cyanide after being subjected to this treatment. In the first investigation of Surinana ore the presence of silver jarosite was suggested and it is possible that some is present, although it appears that this is not the sole cause for the silver being refractory, since after a low-temperature roast some 25 per cent is still insoluble in cyanide. Further, any beneficial results brought about by this treatment can be accomplished equally as well by the use of a solution of ferric sulphate, indicating that oxidation is the effective reaction. By treating the finely ground ore first with a solution of sulphur dioxide and then with a solution of ferric sulphate, 90 per cent of both gold and silver can be extracted with cyanide, suggesting that oxidation as well as a general cleaning up of the metal content is necessary.

Identification of the minerals with a microscope is said to be impossible, although further effort along this line is now being made. In the development of a commercial process from the accumulation of data such as outlined above due consideration must be given to the remoteness of the district as well as to the possible life of the mine.

## References

1. E. R. Richards: Salt Roasting and Cyaniding at Achotla, Mexico. *Eng. and Min. Jnl.* (1928) **126,** 325–329, 370–375.
2. H. P. Allen and W. C. Madge: The Chloridizing Mill of the Standard Reduction Co. *Trans.* A.I.M.E. (1925) **73,** 317.
3. G. H. Dern and T. P. Holt: Ore Roaster. U. S. Patent 1113962 (Apr. 9, 1914).
4. R. E. Head: Physical Characteristics of Gold Lost in Tailings. Page 256, this volume.
5. E. S. Leaver and J. A. Woolf: Cyanide Extraction of Gold and Silver Associated with Arsenic and Antimony in Ores. U. S. Bur. Mines *Tech. Paper* 423.
6. C. A. Schempp: *Amer. Jnl. Sci.* (July, 1923) **6.**

## DISCUSSION

(*C. E. Locke presiding*)

G. L. Oldright,* Salt Lake City, Utah (written discussion).—Mr. Allen's pape marks another advance in chloridizing processes. In his work, chloridizing roasting and leaching with dilute and acidic salt solutions were carried out chiefly as steps preliminary to cyaniding. It was desired first to remove impurities from the ore, and to "free" the gold particles, if the meaning of "free" be extended beyond the mechanical liberation of precious mineral particles to include the cleaning of their surfaces. Mr. Allen suggests compounds of manganese, arsenic, antimony, among the deleterious products that might have been removed, or decomposed by the treatment given. There are many other products soluble in brine or decomposed by acidic ferric sulphate. The U. S. Bureau of Mines[7] learned that part of the gold was made insoluble in cyanide solutions by roasting ores containing lead minerals, particularly if the ore were not roasted at low temperatures and the lead sulphated. After the lead was leached out with acidulated brine, the gold dissolved in cyanide solutions. The "cleaning" or alteration of the surfaces of coated mineral particles that are otherwise freed mechanically so as to make them amenable to treatment by flotation or cyanidation processes is one of the most important and baffling of our present problems.

---

* Supervising Engineer, Nonferrous Metallurgy Section, Metallurgical Division, U. S. Bureau of Mines.

[7] E. S. Leaver, J. A. Woolf and T. A. Jackson: Cyanidation of Calcined Gold Ores Made Refractory by the Presence of Lead Minerals. A.I.M.E. *Contribution* 5 (1933).

# Physical Characteristics of Gold Lost in Tailings

By R. E. Head,* Member A.I.M.E.

(New York Meeting, February, 1936)

Under existing economic conditions, the treatment of gold ores occupies an outstanding position in metallurgical activity. The increased price of gold has automatically brought about a reclassification of old dumps and low-grade orebodies, and many that formerly were considered valueless are now being vigorously investigated and worked. This situation has developed problems that have taxed the ingenuity and ability of metallurgists to the utmost. Some gold ores give a high extraction of gold by standardized methods of treatment; other ores of apparently similar character yield but a relatively small percentage of their gold when treated by the same processes.

## Surface Contamination

The experience gained by microscopic study of numerous gold ores and tailings has shown that there are pronounced differences in the physical characteristics of the minerals composing them, more especially of the gold. Repeated studies of tailings from flotation and cyanidation of gold ores has established the fact that surface contaminations on gold particles are often directly responsible for high gold losses; comparison of gold particles isolated from flotation concentrates and the resulting tailings have showed that the clean gold has been recovered and the tarnished or contaminated gold invariably lost in the tailing. Obviously, it is not possible to make such a comparison of gold ores treated by cyanidation, as the clean gold has been taken into solution; but when the gold found in cyanide tailing has a tarnished or coated surface, one may infer, with a reasonable degree of certainty, that the clean gold has been extracted. This premise is supported by experimental evidence obtained by isolating particles of tarnished gold and exposing them to cyanide solution in small parting cups. In one such experiment, tarnished gold particles picked from a cyanide tailing showed but slight evidence of dissolving at the end of 27 days. In this test, a cyanide solution of 1.6 lb. per ton was used and the leach solution was decanted and renewed every

---

Manuscript received at the office of the Institute Nov. 29, 1935. Published by permission of the Director, U. S. Bureau of Mines. Issued as T.P. 674, February, 1936.

* Microscopist, Intermountain Experiment Station, U. S. Bureau of Mines, Salt Lake City, Utah.

24 hr. The proof of cyanide attack was manifested by a noticeable thinning of the gold particles at the edges (Fig. 1). A rim of a substance that appeared to be gelatinous was visible at the edges of the gold particles, and there is reason to believe that this material encased the entire surface of the gold particles. It is not known whether the gelatinous film is of secondary origin, resulting from a reaction between the cyanide and some substance or substances adhering to the gold surfaces in the form of a coating, or is an original constituent of the surface contamination which has been made visible through the dissolving of a small amount of gold at the margins of the particles.

Visual examination indicates that some phase of oxidized iron constitutes a material part of the coating on gold particles lost in tailing. Warm hydrochloric acid dissolves the iron stain from the surfaces of many tarnished gold particles, and microchemical tests of the solution show the presence of iron. Many tarnished gold particles possess a slightly attractive susceptibility to the field of a magnetic point, which further substantiates the existence of iron in some form. In some cases, this attraction is so strong that an instrument of nonmagnetic metal must be used to remove the gold particle from the magnetic point and mount it on a slide for observation.

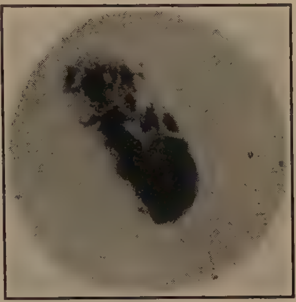


FIG. 1.—PARTICLE OF COATED GOLD GROUND TO 65 MESH. × 100.
Shows progress of gold dissolution and film residual that marks original outline of particle. Black portion is gold and indistinct outline is film.

In analyzing the foregoing statements from a critical standpoint, it should be kept in mind that the greater number of the gold particles examined during the study were of minus 200-mesh size (0.074 mm.), and gold particles as small as 6 microns (0.006 mm.) were isolated, mounted, and examined at magnifications as high as 1020 diameters. This extremely small particle size, together with the limitation of the number of particles available from a given tailing, restrict determinative work on tarnished gold to visual observation and microchemical tests. The time-consuming nature of this kind of work is also worthy of mention, as well as the refinement of the technique required to concentrate and isolate gold from tailing containing from 0.02 to 0.06 oz. per ton.

## SURFACES OF GOLD PARTICLES

Some study has been given to the surface characteristics of minerals, but little to the nature of the surfaces of gold particles, especially where the gold has been difficult to recover. The importance of surface conditions and their functions in flotation are now well established; and, in the field of gold treatment, surface conditions may affect the results obtainable by cyanidation and amalgamation as much, or perhaps more, than in flotation. Inasmuch as gold having tarnished or coated surfaces has been found in appreciable quantities in tailings from the flotation, cyanidation and amalgamation of many difficultly treatable gold ores, certain characteristics that are common in many instances are described.

The microscope shows that the surfaces of gold particles in ores are seldom smooth or crystalline. In approximately 100 samples of tailing gold studied, the surface of the particles was decidedly uneven and pebbly (Fig. 2). Whether this pronounced inequality of surface is due to "working stresses" and pressure applied during oxidation is not known. The low or recessed portions of these "pebbly" surfaced particles were more abundantly coated with extraneous substances than were the high spots. This would occur under conditions of alteration and pressure previously cited. It would also follow, as a natural consequence, that such particles could not be cleaned or scoured to any material extent by grinding or attrition. As a matter of fact, gold particles having "pebbly" surfaces would probably become increasingly contaminated through the attachment of extremely small particles of gangue material, especially if ground in the presence of natural slime[1] substances such as kaolin, sericite, or ocherous iron oxide. Previous microscopic work done

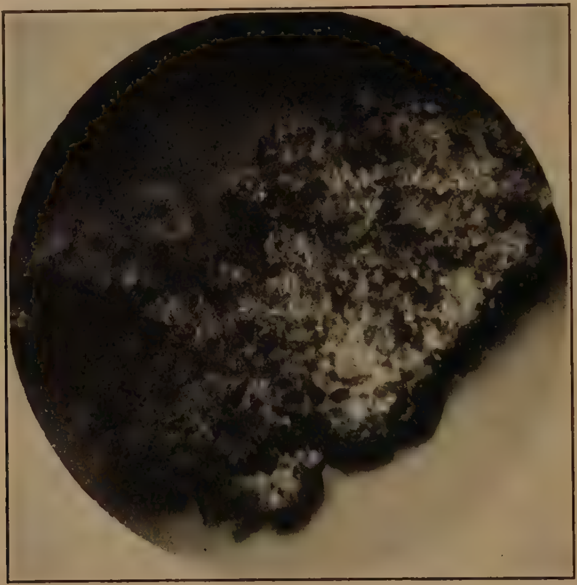


FIG. 2.—PARTICLE OF GOLD GROUND TO 65 MESH. × 220.
Shows both pebbly, irregular nature of surface and difference in film thickness rendered in black and white.

---

[1] G. L. Oldright and R. E. Head: Microscope Reveals Influence of Mill Grinding on Floatability of Gold. *Eng. & Min. Jnl.* (1933) **134**, 228–232.

on Utah Copper ore by the author and quoted in a paper by H. S. Martin[2] showed conclusively that alteration products impressed on the surfaces of chalcocite definitely interfered with their flotation and resulted in a material increase in copper loss.

At some plants using ore that is composed largely of quartz and feldspar, and grinding to 90 per cent minus 200 mesh, the gold recovered in the tailing launders is all of the tarnished and coated variety, the clean, floatable gold having been removed in the base-metal concentrate. The gold particles have been exposed to more than the usual amount of grinding and attrition, which has failed to clean the surfaces, as evidenced by microscopic examination. The evidence shows that the agencies of volume change and pressure have compacted the secondary minerals around the gold in the form of a shell, virtually impenetrable to water or cyanide solution in any reasonable period of time. Such particles obviously do not cyanide or amalgamate and, as the coating is usually of a nonmetallic nature, do not float. Where the gold surface is but partly slimed over, the floatability becomes problematical, depending on the percentage of clean surface on a given particle. The rate of dissolving in cyanide solution likewise is decreased proportionately, but it may be sufficiently rapid to attain completion in the normal time of cyaniding treatment.

## Tarnished Gold

It is not difficult to visualize and understand the existence of slime coatings on gold particles and their role in contributing to tailing losses. Another phase of surface contamination, however, is more difficult to visualize, although its function in causing gold losses is just as pronounced and positive as are the slime coatings. Microscopic study of free gold particles isolated from flotation, amalgamation and cyanidation tailings has shown conclusively that their surface is filmed over or coated with some substance or tarnish that renders these particles inert to reaction with the agents employed to recover them. The existence of tarnished gold in orebodies probably has not been generally recognized, but the significance of tarnish in relation to recovery of the gold is important. Comparison of the surface of gold particles recovered in a flotation concentrate with that of particles lost in the tailing from a certain plant has shown easily discernible difference in color. Particles in the concentrate have clean and reflective surfaces, but those in the tailing showed surface tarnish and discoloration. This condition has been found to obtain in a number of cases, therefore the conclusion that the tarnish contamination of gold particles is responsible for their failure to float is logical. Acceptance of the theory that reactions of a delicate and selective nature take place between flotation agents and the mineral surfaces suggests that tarnished gold particles and those with clean, bright surfaces might behave differently in a flotation circuit.

---

[2] H. S. Martin: Microscopic Studies of Mill Products as an Aid to Operation at the Utah Copper Mills. *Trans.* A.I.M.E. (1930) **87**, Milling Methods, 459–460.

There is no material difference of opinion regarding the floatability of normally clean gold particles. In common with cyanidation and amalgamation, flotation will make satisfactory recoveries of clean gold particles in the size ranges to which the process is adaptable. The tarnished and coated gold particles present an entirely different matter for consideration, as their recovery involves floating the substances that coat the gold. For example, the recovery of gold particles entirely encased in oxidized iron presupposes floating the particular type of iron oxide that constitutes the coating. If the coating is made up of silica or carbonaceous material, the hypothesis remains the same—the surface coating must be floated in order to recover the gold particle it encases. Regardless of the composition and nature of any film, tarnish, or coating on the surface of gold particles, it is logical to reason that their behavior when exposed to cyanide, amalgamation, or flotation will not parallel that of normal, clean gold under the same conditions. It follows, therefore, that any reagent or combination of reagents cannot be heralded as a panacea for overcoming the difficulties involved in treating refractory gold until definitely proved in each individual case. The same assumption holds true with regard to variations or innovations in cyanide or amalgamation practice.

Since surface tarnishes or films exert fully as deleterious an effect on gold recovery as do the compacted slime or other foreign encasing agents, a brief description of their appearance and characteristics is given. As the name implies, tarnish is surface discoloration that is formed on the gold surfaces by various agencies. It may be caused by the mechanical adhesion of substances surrounding the gold particles, or it may be due to reactions between the impurities in the gold and the various agencies, chemical and otherwise, that are involved in ore deposition and alteration. Tarnish undoubtedly is of varying thickness, as evidenced by the extent of deviation in color from that of normal clean gold. When mounted and examined microscopically at high magnifications, varying thicknesses of film are evidenced by the differences in color refraction from various portions of a given particle. Additional proof of the pebbly surfaces of gold and the building up of extraneous material in the depressions is shown at high magnifications, by the color refraction produced and the actual visualization of film thickness. These tarnish films are so thin the visual indication of their existence is possible only by comparison with normal clean gold surfaces or by observation of highly magnified surfaces. Predictions concerning the behavior of filmed or tarnished gold particles in amalgamation or cyanide solution are unreliable because the gold surfaces are not always completely covered. In such instances, solution contact takes place and the gold dissolves. In flotation, however, the element of time exposure to recovery agencies is relatively so short that even partly tarnished particles become difficultly floatable. This may explain why cyanidation of flotation tailing often extracts a material portion of the gold content.

From the standpoint of flotation research, it is highly desirable that the exact nature and composition of tarnish films be known. This information would be of value in developing or selecting flotation reagents possessing properties necessary to promote the recovery of filmed gold. The existence of iron has been proved conclusively in many cases, but experimental evidence indicates that it is but one of the contaminants, inasmuch as its removal by hydrochloric acid did not completely remove the film from certain particles tested. It is believed, however, that some one of the many oxides of iron in the ferric condition often constitutes the secondary or outer film, because tarnished gold particles from certain refractory ores were blackened by a sodium sulfide solution.

It is believed that the contaminants that make up the tarnish films will vary considerably in different localities because of differences in the physical and chemical natures of the rocks and minerals associated with the gold. Iron, however, has been found on or in the tarnish films of all particles tested. If the iron salts or compounds comprise the outermost portion of the film on refractory gold particles, the floatability of such particles will be governed by the establishment of conditions best suited to recover the particular type of iron salt present. The existence of another film of different composition underlying the outer film may or may not be a modifying factor.

## SPECTROGRAPHIC STUDY

Attempts have been made to learn more through spectrographic studies about the impurities in and on refractory gold particles. The equipment available was somewhat mediocre, which imposed certain limitations in the range covered. In the range above 3600-A, silver, iron, lead, manganese, aluminum, and titanium were indicated. (The term "indicated" is used pending substantiation of these findings on a larger quartz-prism type of instrument.) Although spectrographic study of contaminated gold will show the elements present, the conclusive differentiation between those present as films on the surface and those combined or alloyed with the gold itself would require that comparisons be made between records of tarnished gold particles and duplicate particles that had been treated with cleansing agents to remove all surface coatings.

## OXIDIZED AND PYRITIC ORES

The problem of filmed and coated gold is largely represented by the oxidized and semioxidized ores, which also include waste dumps and tailings from former operations. Difficulties in the cyanidation of pyritic ores and concentrates usually have been of a different nature. It is an accepted fact that some gold-bearing pyritic ores can be successfully treated by a cyanidation without resorting to excessively fine grinding; but others must be ground to the extreme limits of economic practice. This indicates a difference in the porosity of the host pyrite, which governs the permeability of cyanide solution and automatically limits the extraction of gold. Gold can and does occur in flakes of such small size on the crystallographic planes of pyrite that crushing to the extremes of economic practice will not liberate all of it. This explains why a preroasting treatment has been so beneficial to certain ores and pyritic concentrates that did not cyanide satisfactorily in the raw condition. Properly conducted roasting in such cases usually rendered the pyrite sufficiently porous to permit the cyanide solution to come in contact with and dissolve the gold. Tarnished gold particles have been found occasionally in tailings from the combined flotation and cyanide treatment of pyritic ores, but the percentage of the total gold lost as tarnished particles is much less than that lost as locked or included particles. As the costs of grinding and handling slimed material have established definite limitations to the degree of grinding practicable, gold locked in compact, impermeable pyrite will be lost, except when the expense of roasting is justified by the additional amount of gold possible of extraction.

## Processes for Refractory Ores

It is quite likely that the characteristics of contaminated gold particles in the refractory ores differ sufficiently to preclude the possibility of developing a process other than smelting that will have universal application and yield consistently satisfactory results on all refractory gold ores. The situation, therefore, resolves itself into a matter of determining what process or combination of processes is best suited to extract the greatest amount of gold from a given ore at the lowest cost.

After summarizing and considering the problem of recovering contaminated gold, several possible methods of attack present themselves.

1. The possibility of finding some procedure for removing the surface contamination, thus conditioning the gold for treatment by cyanidation, amalgamation or flotation.

2. Utilizing the surface coating as a base for producing a more easily floatable surface through the agency of a suitable reagent or combination of reagents.

3. The development of reagents that will selectively float the substances that form the coatings on refractory gold particles.

4. The employment of refined gravity methods specifically designed and placed in mill circuits to aid gold recovery.

5. The perfection of tailing launder design and operation as scavenging devices.

## DISCUSSION

*(Arthur F. Taggart presiding)*

A. W. Hahn,* Salt Lake City, Utah (written discussion).—Not all of the gold found in old cyanide tailings is tarnished, as evidenced by the high-grade crusts harvested from the surfaces of tailings at several places. This gold, in desert localities, was probably brought into solution by the concentration of the cyanide remaining in the tailings pulp, as it was sluiced from the filters to the tailings pond, and through capillarity worked its way to the surface of the tailings through a varying period of time.

Some of the gold recovered from old cyanide tailings was probably lost in the original milling process through its occlusion in sulphide copper and iron minerals, or a combination such as chalcopyrite, but through the agencies of time and oxidation, the combination was destroyed and the gold became amenable to leaching with dilute cyanide solutions. If the original milling operation was a combination of amalgamation and cyanide treatment some of the gold losses may have been in amalgam escaping from the plates and traps to the tailings pond, in an extremely fine state of subdivision, and this combination may also have oxidized to the extent of making the gold soluble in cyanide solution when air-agitated by either pumps or agitators. The gold left in the cyanide tailings after re-treatment by cyanide is probably "coated" gold.

The methods of attack cited by Mr. Head are of particular interest, and test work along the lines suggested have been tried and in some instances proved successful in the laboratory. An ore from Oregon, containing 0.40 oz. gold and 1.0 oz. silver, by microscopic examination was found to be present in the following forms: (1) bright free gold, (2) tarnished free gold, (3) occluded in the pyrite, (4) masked in the graphitic carbon flakes present, (5) probably combined with silver sulphide (argentite). It was treated to separate the various forms, by stage flotation, with the following results:

| Calculated Heads | | Concentrate No. 1 | | Concentrate No. 2 | | Concentrate No. 3 | |
|---|---|---|---|---|---|---|---|
| Au | Heads | Au | Ag | Au | Ag | Au | Ag |
| 0.452 oz. | 1.37 oz. | 3.06 | 24.04 | 2.12 | 3.68 | 2.60 | 1.70 |
| 100.0% | 100.0% | 24.1% | 62.3% | 44.1% | 24.9% | 19.5% | 4.1% |
| Reagents........ | | CaO, 8 lb.<br>KCN, ½ lb. B.M.<br>No collector<br>Frother, ¼ lb. D-23 | | Z-6, 2 lb.<br>D-23, 2/10 lb. | | $H_2SO_4$, 25 lb.<br>Z-6, 1 lb.<br>D-23, 2/10 lb. | |

Concentrate No. 1, when the iron pyrite was depressed by both lime and cyanide, was floated with a frother only, and a very selective frother, yet 24.1 per cent of the gold and 62.3 per cent of the silver was removed, which was occluded or attached to the graphitic carbon.

Concentrate No. 2 contained the untarnished gold and pyrite.

Concentrate No. 3 contained the tarnished gold and pyrite that was activated by conditioning with sulphuric acid before floating.

---

* Metallurgist.

There appears to be an unexplored field for differential flotation of gold ores, the term "differential" referring in this case to the various forms of gold present in the ore, which present different flotation characteristics. In this particular type of work, the microscope is invaluable.

A trained microscopist is required for this work, as the isolation of the gold and mineral particles is a special branch requiring infinite patience. Mr. Head is to be congratulated for his excellent work and presentation of a valuable contribution to an important research.

R. E. HEAD.—It is true that not all gold in old cyanide tailings is tarnished or coated at the present time. Many of these dumps have been exposed to the complex reactions incident to weathering over a long period of time—up to 20 years or more. This constitutes a cycle of conditioning which in many cases has been highly beneficial in cleaning or otherwise making the gold amenable to recovery by cyanidation or other methods of treatment.

In old dumps such as those at Mercur, Utah, which are said to contain 3,000,000 tons with an estimated gold content of approximately 0.07 oz. per ton, the value is sufficiently great to pay re-treatment costs provided a satisfactory recovery of the gold can be made.

The immediate importance of the tarnished-gold problem lies in present-day practice. Even with the advances that have been made in handling minus 200-mesh pulps, in which a high degree of gold liberation has been attained, losses up to $4000 per day at a single plant are being sustained. Although the loss per ton is relatively small, rarely exceeding 0.01 oz. in gold, the aggregate in large-tonnage operations is enormous. This loss in tarnished gold is supplemented materially by that sustained in numerous small operations showing tailing losses up to 0.04 oz. per ton. Most of this loss has been shown by microscopic study to exist as liberated, tarnished gold.

Since free gold particles are being lost, there is a chance of working out a means for their recovery. The chief importance of the problem lies in the fact that present-day gold losses occur in tailings of such low metal content that re-treatment seems an extremely remote possibility.

# Electrocapillary Amalgamation

By Orson Cutler Shepard,* Associate Member A.I.M.E.

(San Francisco Meeting, October, 1935; New York Meeting, February, 1936)

The term "electrocapillary amalgamation" is used in this paper to designate amalgamation processes that depend upon electrocapillary phenomenon; i.e., the action of an electric current upon the surface tension of mercury at the contact with aqueous solutions. Electrocapillary amalgamation is selected as a name for these processes because the electrocapillary phenomenon has been found to be the effective agent in the use of sodium amalgam, as well as in the various processes using an electric current from a source outside of the amalgam. Amalgamation processes that depend upon supplying an electric current to the amalgam from an outside source, such as batteries and generators, have previously been called electrical amalgamation processes.

There has been a tremendous amount of experimental work done on amalgamation processes involving the use of an electric current, as shown by the large number of patents issued on these processes: the earliest in 1885 and the latest in 1934[1]. Regardless of all the experimental work, the fundamental principles causing the operation of electrocapillary amalgamation processes have not been described. The explanation usually given is that an electric current keeps the amalgam bright and clean. Patent No. 328532 states:

> It is well known that when amalgam plates are used for collecting gold and silver from their ores the surfaces of these plates are liable to become tarnished or sickened by certain substances contained in the ores or in the current of water which is employed to carry the ore over the plates, and that in this condition they are unfitted for amalgamating the particles of gold and silver. To prevent this and to keep the surfaces of the amalgamation plates always bright and in a better condition for catching and amalgamating the particles of gold and silver I employ electricity in the following manner: . . .

A similar explanation is given 49 years later, in patent No. 1953364:

> The sodium (Na) ions lose their charge at the cathode becoming sodium atoms, which do not react with the electrolyte, but follow the grounded electrical current through the mercury body producing in their passage sodium amalgam and liberate themselves in the amalgamation compartment when brought in contact with the fed

---

Manuscript received at the office of the Institute, Oct. 3, 1935. Issued as T.P. 676, February, 1936.

* Assistant Professor of Mining and Metallurgy, Stanford University, Palo Alto, Calif.

[1] References are at the end of the paper.

pulp and form sodium peroxide, this in sequence, forms sodium hydroxide and gasses with feed material, and has the distinct effect of cleaning the mercury and the metals, metalloids and colloids in the material under treatment.

The only mention found that surface tension is involved in amalgamation processes that use an electric current appears in a description of the McBride process[2]:

> The successfulness of its action is based principally on destroying surface tension. The very reason mercury flows so readily is due to the fact that because of its density and surface character, it provides for pronounced surface tension. The tiny speck of gold, even though of much greater specific gravity, does not enter the mercury when in contact with it because the surface tension of the mercury does not permit it. The phenomenon is like that of a needle floating on the water. Besides the surface tension affects the particles of gold and silver and even more so, the platinum.

It is believed that electrocapillary amalgamation processes have not found much use because the best conditions of operation were not discovered, through a lack of understanding of the principles involved. R. C. Canby[3] says:

> Intensive amalgamation consists in the use of aids to contact or union of the precious metals and the mercury, e.g. passing a small low-voltage electric current through the plate; placing iron bars on the plate and milling in salt water (sea water): placing plates on the walls of a centrifugal machine: grinding in the presence of mercury, etc. Except for the last expedient, the results do not justify the expense.

The cost of electrocapillary amalgamation should be slight because not more than 0.07 amp. per sq. ft. of plate area is required and the voltage is low. Consequently, if a small additional recovery were made, the process would be profitable, particularly at gold mines where amalgamation is the main recovery process.

## Electrocapillary Phenomenon

Electrocapillary phenomenon exhibits a characteristic variation in the surface tension of mercury at the contact with solutions of certain electrolytes, when the mercury is polarized with a negative potential. The curve obtained by plotting the surface tension of the mercury as ordinate and the potential of the mercury as abscissa is called the electrocapillary curve. This curve has been known and studied since about 1873, when Lippmann devised the capillary electrometer. A typical electrocapillary curve[4] is shown in Fig. 1. The surface tension, mercury-electrolyte, characteristically increases to a maximum with increasing negative polarization of the mercury, and then decreases with further increase in polarization. Koenig[5] has derived the equations for the electrocapillary curve by thermodynamic reasoning.

The surface of an ordinary amalgamation plate can be varied in tension by electrical polarization in a manner similar to the electrocapillary curve for liquid mercury. This can be seen from the fact that the angle of contact $\theta$ of an air bubble with the amalgamation plate increases to a maximum with increasing negative polarization of the amalgam, and then decreases with further increase in polarization. In this case the solution-air and amalgam-air surface tensions remain unchanged, so that as the amalgam-solution surface tension increases the bubble spreads out on the amalgam, making a greater angle of contact. The relation just described follows from the well-known equation:

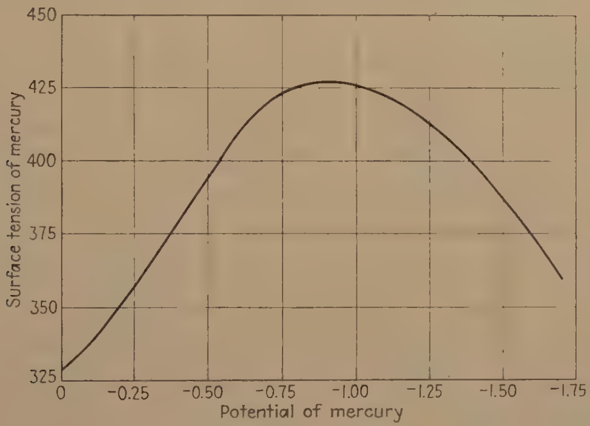


FIG. 1.—TYPICAL ELECTROCAPILLARY CURVE. (*After Freundlich.*)

$$\text{Tension amalgam-air} = \text{tension amalgam-solution} + \text{tension solution-air} \cos \theta$$

A curve obtained by plotting the angle of contact of an air bubble on an amalgamation plate at various potentials is similar to the electrocapillary curve.

## EFFECT OF ELECTROCAPILLARY PHENOMENON ON AMALGAMATION

In order to determine the effect of electrocapillary phenomenon on amalgamation, a small strip of amalgamated silver foil was used as an amalgamation plate in a beaker containing a solution of sodium chloride (½ gram per liter). The amalgamation plate was connected to a variable source of negative potential; and a platinum wire, connected to the positive source of potential, was placed in the solution for an anode.

Starting with no potential between the amalgamation plate and the anode, and with gradually increasing increments of potential, small pieces of gold were dropped on the amalgamation plate and the rate of amalgamation was noted. The gold particles amalgamated slowly until the polarization giving maximum surface tension was passed. Beyond the point of maximum surface tension, amalgamation of the gold was extremely rapid. It was observed that when the plate was dressed with excess mercury the excess flowed away from the position on the plate nearest the platinum anode, leaving the amalgam dry in the region near the anode. If a particle of gold was dropped on the dry amalgam, the excess mercury would flow to the gold particle and engulf it immediately. A piece of pyrite would also cause the excess mercury to flow to it. The mercury would float the pyrite up from the plate and sometimes cause it to slide to one edge of the plate and drop off. Except when an excessive voltage was used, mercury or amalgam did not cling to barren pyrite. Even when the plate was dressed very dry, gold particles amalgamated instantly at a polarization exceeding the maximum of the electrocapillary curve. Particles of gold continued to amalgamate rapidly as the voltage was increased. However, when pyrite or other sulfide minerals were present, the plate became stained if too high a voltage was applied.

Tests were made with two telluride specimens: calaverite from Cripple Creek, Colo., and a specimen containing a mixture of various telluride minerals from Kalgoorlie, Australia. Neither mineral amalgamated when the plate was not polarized. With a polarization slightly exceeding the maximum of the electrocapillary curve, the calaverite amalgamated rapidly and without staining the plate. The mixed telluride specimen from Kalgoorlie amalgamated slowly and the plate was darkened near the mineral particle. Pieces of silver amalgamated in exactly the same manner as gold particles.

In order to test electrocapillary amalgamation on an actual ore, a small silver-foil plate 1¼ in. wide by 10 in. long was constructed. In the first tests three platinum wires were fastened transversely about ⅛ in. above the plate for anodes. A sample of gold ore from a mine near Jackson, Calif., was ground dry in a ball mill and then screened through a 100-mesh sieve to remove coarse gold. The coarse gold was removed, so that small samples would give consistent assay results. Samples containing 150 grams of this ore were agitated in a dilute solution of sodium chloride and allowed to flow slowly over the amalgamation plate to determine the recovery of gold when the plate was polarized and also without electrical polarization. In every case a higher recovery was made when the amalgam was polarized negatively with a potential slightly greater than the maximum of the electrocapillary curve. When the potential was increased as much as a volt beyond this point, pyrite became embedded in the amalgam and the plate became tarnished. It was noticed that when the plate was polarized at the best voltage, a large amount of the gold recovered had collected just below the anode wires. Consequently, it appeared that a larger number of anode wires placed close together would give even better electrocapillary amalgamation.

A new set of anodes was constructed for the amalgamation plate used in the previous test. This set consisted of 19 transverse, chromel wires mounted ½ in. apart in a frame that could easily be removed for dressing the plate. A sample of the same minus 100-mesh ore gave a recovery of

29.7 per cent when run over the plate with the new anodes and without any applied potential. When a sample of the same material was run over the plate six times in succession without potential the recovery was raised to 32.6 per cent. This recovery is low compared with that made by amalgamation in mills operating on a similar ore. The low recovery is believed to be due to the removal from the sample of a considerable part of the easily amalgamable gold in the plus 100-mesh material taken from the sample before making the test.

When the plate was polarized with a potential of 1.25 volts between plate and anodes, a sample passed over the plate once gave a recovery of 28.8 per cent. This potential was not sufficient to raise the surface tension to the maximum of the electrocapillary curve. At 2.0 volts the maximum of the electrocapillary curve was passed and the recovery was raised to 62.9 per cent. A further increase in potential to 2.25 volts gave a recovery of 64.8 per cent. When the same sample was passed over the plate six times in succession with a voltage of 2.25 volts, the recovery was 72.6 per cent. Tests at higher voltages were not made, since it had been found that even though the results were good in a short test, the plate soon became tarnished so that the recovery gradually decreased unless the plate was frequently dressed.

It was then decided to try tests on a larger scale. A silver-plated sheet of copper 1 ft. wide by 5 ft. long was procured for this work. The plate was mounted on a slope of 1½ in. to the foot, so that the discharge from a mechanically fed, laboratory ball mill would flow over it. A wooden frame was constructed to hold 28 carbon rods transversely across the plate just low enough so that the carbons touched the top of the pulp stream. Carbon anodes were substituted for chromel wires, because the chromel showed some corrosion even in the short time it was used.

The salt-solution electrolyte used in the small-scale tests was made up with distilled water. There was not sufficient distilled water available to operate the 5-ft. plate. Consequently, regular tap water, from wells, was used. It was found that the amount of salts in the well water was more than desired and that no additional salt needed to be added. When amalgamation tests were made using well water and electrically polarizing the plate, the results were unsatisfactory. The plate became coated in a few hours with a white deposit that prevented contact of the gold with the amalgam. An analysis showed that the white deposits consisted of calcium carbonate. The calcium was derived from the well water because the deposit formed on the plate when water alone was present. In order to avoid the difficulty with calcium salts in the well water, a water softener was used to exchange sodium for calcium. The softened well water contained such a large amount of salts that the amalgamation plate could not be polarized quite as much as in the first small-scale tests. Polarization is measured by the potential between the amalgamation plate and a calomel electrode in the electrolyte above the plate. The potential between the anode and plate includes anode polarization and the *IR* drop of the electrolyte, as well as the polarization of the plate. The potential measured with a potentiometer between the plate and a saturated calomel electrode in the first test with chromel anodes was 1.29 volts, when the potential between anode and cathode was 2.25 volts. With the 5-sq. ft. plate and softened water, the polarization was 1.19 volts when the potential between anode and cathode was 3 volts. With this voltage the current was 0.35 amp., or 0.07 amp. per sq. ft. of plate area.

Ore from a mine at Grass Valley, Calif., was crushed through a 20-mesh screen and then fed to the laboratory ball mill with softened water. The ball-mill discharge was further diluted with softened water and then run over the 5-sq. ft. amalgamation plate. The run was continued for 4 hr. at the rate of 25 lb. of ore per hour. At every other 15-min. interval the plate was electrically polarized with 3.0 volts between anodes and the plate. Separate samples were taken during the intervals when the plate was polarized and the intervals without polarization. An average of the samples taken during polarization gave a recovery of 87.5 per cent of the gold. The average of the samples taken when the plate was not polarized gave a recovery of 83.0 per cent.

## Explanation of Action of Electrocapillary Amalgamation

When an amalgamation plate is given a polarization slightly exceeding the maximum of the electrocapillary curve, the polarization is greatest on the plate in the region near the anode. Consequently, the surface tension of the mercury and amalgam is low near the anode. At a greater distance from the anode the polarization is less and the surface tension is high. The excess mercury flows to the regions of high surface tension, leaving the amalgam dry in the region near the anode.

Mercury and amalgam have an exceptionally high hydrogen overvoltage. If this were not the case, hydrogen would be evolved from the plate before a polarization sufficient to lower the surface tension could be reached. When a particle of gold that has a low hydrogen overvoltage touches an amalgamation plate that is polarized beyond the maximum of the electrocapillary curve, hydrogen is evolved from the gold and the polarization of the amalgamation plate is slightly lowered near the gold particle. This raises the surface tension of the amalgam near the gold particle, and draws mercury up and over the gold, amalgamating it instantly. As soon as the gold is amalgamated, its hydrogen overvoltage is high and the plate returns to its original condition.

Probably a part of the increased ease of amalgamation caused by polarizing an amalgamation plate is due to the fact that the surface tension of the amalgam on the plate has different values at different places on the plate, depending upon the proximity of the anode. If any coating that tends to lower the surface tension of the amalgam occurs on the plate, it will automatically move to the places on the amalgam having the highest surface tension, in order that the system may come to equilibrium with the least free energy. This tends to maintain horizontal bands across the plate that are free from surface contamination.

After the explanation of electrocapillary amalgamation was developed, it was suggested that probably the effectiveness of sodium amalgam was due to the electrical potential generated from oxidation of the sodium. To test this idea, a small silver-foil amalgamation plate was placed in a beaker of water, and the effect on the amalgamation of gold of adding dilute sodium amalgam was observed. Sodium amalgam caused excess mercury to flow to a gold particle and amalgamate it immediately, in a manner exactly similar to electrical polarization. A saturated calomel electrode was then introduced into the beaker, so that the potential between the plate and the calomel electrode could be measured. When sodium amalgam was added to the plate, the potential increased to 1.8 volts. In less than one minute the potential dropped to nearly zero, owing to oxidation and removal of the sodium. As soon as the potential dropped to less than the maximum of the electrocapillary curve, the rate of amalgamation of gold was no faster than before sodium amalgam had been added. It is believed that this evidence shows conclusively that sodium amalgam aids the amalgamation of gold by causing electrical polarization of the amalgamation plate.

## Conditions Suitable for Electrocapillary Amalgamation

Electrocapillary amalgamation is suited to the recovery of free gold from ores that do not contain large amounts of sulfide minerals, and where the water used in milling is comparatively pure. If the water is exceedingly pure, a small amount of salt or sulfuric acid should be added to make an electrolyte. Probably considerably less than one pound per ton of solution would be sufficient in most cases. Salts containing cations that deposit on the mercury at low voltages are detrimental. Large amounts of sulfide minerals lessen the electrocapillary effect, because the polarization of the plate cannot be maintained when it is covered with sulfide minerals.

The voltage is a critical factor in the success of electrocapillary amalgamation. It must be sufficient to give the plate a polarization slightly greater than the maximum of the electrocapillary curve. A polarization of from 0.2 to 0.5 volts greater than the maximum of the curve gave the best results. Higher voltages were satisfactory for a short time, but if continued caused the plate to become tarnished and dull, through electrochemical action on constituents of the ore. The actual voltage required between anode and cathode varies with the substances present in the mill water and the material used for anodes. Because of this, the voltage must be determined for each particular case.

It is believed that with suitable conditions electrocapillary amalgamation will recover more gold than simple amalgamation on a plate that is not electrically polarized. In the tests described, electrocapillary amalgamation did not make as high a gold recovery as simple amalgamation followed by cyanidation. Consequently, the field for electrocapillary amalgamation is probably limited to placer gold and to that from small lode mines where the equipment cost of a cyanide plant is not justified.

## REFERENCES

1. U.S. Patents 328532 and 1953364.
2. Mining in California. Report of State Mineralogist, April, 1932, 160.
3. A. F. Taggart: Handbook of Ore Dressing, 961. New York, 1927. John Wiley & Sons.
4. H. Freundlich: Colloid and Capillary Chemistry, 287. New York, 1922. E. P. Dutton and Co.
5. F. O. Koenig: Thermodynamics of the Electrocapillary Curve. I—The General Equations. *Jnl. Phus. Chem.* (1934) **38,** 111; II—The Variation of the Electrocapillary Curve with Composition. *Idem,* 339.

## DISCUSSION

(*Arthur F. Taggart presiding*)

E. A. HERSAM,* Berkeley, Calif. (written discussion).—This work needs much attention and needs to be encouraged, as does all of this investigative work on a small scale. I am one of the believers in the similarity between small-scale work and large-scale work when we know what the large-scale work is. Small-scale work is definite; large-scale work is erratic and the conditions are sometimes not fulfilled. The trouble is not with the detail but with the mastery of uncontrolled conditions met in practice. These are things other and beyond the purposes of merely scientific investigation.

Dr. Shepard has made a keen investigation of some critical issues, and in this we must not be too sanguine. We must not overlook the long-time promise of something that has been before us all for many years in many applications, and analogous ways. It has been fruitless, but that, however, must not discourage us from attempting to attain it by this very direct means of electric potential.

Of course, there is no difference between the action by electric potential and chemical action. That is found all through our processes. The chlorination of water can be done electrolytically or it can be done by the addition of chlorine, and there are many other processes; for instance, precipitation of gold from cyanide solutions by electrolytic action. It could be done electrolytically but practically, in its application, it is cheaper to carry the electric potential in the form of zinc to the cyanide solution and put it where we want it, rather than by electrodes, which we have attempted so long and so arduously to apply.

In electric-potential aid to amalgamation there are a good many erratic conditions still to overcome. There is electrolysis with very variable mine waters and mill waters. The anions that develop from electrolysis and get into the electrolyte and the pulp and undo below all that was accomplished above, must be disposed of. We still have to prove that the gold that is favored by electrodeposition would not deposit either of its own accord, if it had a little more time, or for other reasons. Gold is gold. If it is clean, it will deposit automatically because of the terrific force of gold and mercury to alloy. Always such physicochemical processes occur when alloying or amalgamation occurs.

---

* Professor of Metallurgy, University of California.

These are things that must be proved in practice following such significant analytical thought as Professor Shepard has attempted in this research.

R. GAHL, Tirapata, Peru (written discussion).—Professor Shepard has rendered a decided service to gold metallurgists by investigating the influence of the electric current on the rate at which amalgamation proceeds when gold particles are brought in contact with mercury, and by publishing the results of his investigation. So far information on this subject, although plentiful, has been confined to the patent specifications of inventors and therefore has not been entirely unbiased. The publication under discussion has certainly improved the understanding and has facilitated the technical application of this most interesting electrochemical process.

# Modern Trends in Classification

By C. K. McArthur*

(New York Meeting, February, 1937)

The subject of classification is so broad that this discussion is confined to what the author believes is of prime importance in connection with proper grinding and classification.

The years past have witnessed many noteworthy changes in fine grinding and classification, which have been accompanied by a readjustment of ore-dressing flowsheets for the preparation of better ground and/or sized products at an expenditure of less power, steel and maintenance than formerly. Nowhere in the industry is more being done in the way of experimental work to lower costs than in grinding circuits, because, at best, grinding costs are high. Recent years have indicated that, on the average, finer grinding has a real application. Without careful preparation of the process feed, no operation can be highly efficient or successful.

In an earlier paper, the findings of an extensive survey at representative concentrators were presented[1]. Also, in the year of 1935, a technical discussion was given by Dr. J. V. N. Dorr (Some Notes on Classification Trends in America) before the Chemical, Metallurgical and Mining Society of South Africa. In both papers mentioned, much has been said regarding flowsheets, grinding and classification. The author is very familiar with these papers, having had considerable to do with the actual operation of the flowsheets, as well as large mills and classifiers in the work described. Some data from the second paper have been included in the following discussion.

## Circulating Load

In this particular paper it seems advisable to deal with the classification phases of the work that to a major extent govern the success of any closed-circuit grinding unit.

The question has often been asked in connection with a closed circuit: "What circulating-load ratio should be carried?" This is really an

---

Manuscript received at the office of the Institute Feb. 15, 1937. Issued as T.P. 815 in Mining Technology, May, 1937.

* Manager, Canadian Division, The Dorr Co., Inc., Engineers.

[1] J. V. N. Dorr and A. D. Marriott: Importance of Classification in Fine Grinding. *Trans.* A.I.M.E. (1930) **87**, 109.

ambiguous question and one that will lead to great difficulty if not properly considered. Where one really does arrive at the proper ratio to produce the optimum result, it is entirely dependent on the tonnage and character of original feed; that is, new feed coming to the circuit. In other words, the important question should be: "What total tonnage of original feed plus rake product should be fed to the mill?" When the problem is considered in this manner, it takes on a new aspect.

There is available in every grinding unit an effective volume through which feed will pass, which, if properly utilized, will lead to increased capacity. However, if the tonnage of total feed becomes excessive for the total volume, the mill will "choke"—in other words, become so filled with granular feed that the contents refuse to flow through the mill and discharge opening. This is a common sight on test work where heavy tonnages are being crowded through a mill so as to determine maximum grinding efficiency. Changing the dilution of the pulp in the mill will not remedy the congestion. The available volume of the mill has been taxed to capacity, and the stoppage is due to overloading.

Let us now consider how different it is to continue to discuss our grinding problem in terms of circulating-load ratio, rather than tons of total feed. On many ores where fine grinding is completed, large mills are required to handle a relatively small tonnage. Assume that a given ball mill will grind to 150 mesh 200 tons per day when loaded for maximum efficiency. With this tonnage of original feed a good feed load might be 200 tons original feed plus 3200 tons classifier sands—or a total of 3400 tons. This, of course, would give a so-called circulating-load ratio of 16:1.

In the same plant a problem could be set up whereby the identical size and type of a mill might be called upon to do primary work, thereby grinding to 14 mesh. With the grind as coarse as 14 mesh, the given mill would probably handle 600 tons of original feed. If anyone should say that a circulating load of 16:1 is required, this would mean 9600 tons of classifier sands, or a total tonnage of feed to the mill amounting to 10,200 tons. This seems to open up a field for thought. In all likelihood, in primary work the ratio of circulation should be less than for the problem in which the grind is much finer, for it does seem very much out of line to see in one case 3400 tons of total feed going into the mill and in another 10,200 tons going to the same size of grinding unit. With these conditions known, thought has been given the problem from the standpoint of total tons of feed per cubic foot of effective volume in the mill.

In most recent work on grinding problems, very attractive increases have been obtained by using the heavy-duty Dorr classifier, thereby loading the mill and throwing some light on the thought mentioned above. In considering the tons of original feed going to the grinding unit, it is quite apparent that if the tons of original feed are high, a low circulating-load ratio can better fill the effective mill volume than will a higher circulating-load ratio on work in which the tons of original feed are limited. It is to be understood that the mesh of grind naturally determines the feed rate to the mill.

In reviewing several important grinding problems handled recently in which the heavy-duty Dorr classifier was used in the closed circuit for providing large sand loads, it is interesting to see that the total tons of feed to the grinding unit have fallen between the range of 14 to 20 tons per cubic foot of mill volume. Furthermore, in these cases, the circulating-load ratio has been from 4:1 to 9:1. As a matter of fact, at one very large plant in Canada, where grinding in a pilot unit is being completed to 48 mesh by means of a large mill and a heavy-duty Dorr classifier with less than 5.0 kw-hr. per ton, the circulating-load ratio does not average more than 5:1. However, in this particular case the total tons of feed going into the grinding unit amount to approximately 8400 tons per 24 hr. With such a feed the mill is handling a large tonnage per cubic foot of volume, and still the ratio of circulating load through the mill is not high. The rate of flow, however, is rapid, and really means that the mill is being crowded to a point where it will maintain its maximum grinding efficiency. With a lower sand tonnage on the FX rakes, the grinding curve falls off and with too much additional sand the mill becomes sluggish until it finally "chokes," at which time the pulp refuses to flow through the mill and out of the discharge opening.

When further considering the total tons of feed, as compared to the effective mill volume, does it not seem logical that perhaps still better grinding efficiency can be obtained at higher loadings per cubic foot? This would, of course, call for a redesigned grinding unit. In addition to this, the pulp-flow capacity is greatly affected by the nature of the ore and particle sizes; i.e., one grinding mill is known to have been loaded with as much as 30 tons per cubic feet of volume and still functioned well.

With special reference to feeding grinding mills with a satisfactory tonnage of total feed, a brief description of work conducted in an important South American plant may be of interest. This concentrator investigated thoroughly the possibility of increasing the total tonnage of ball-mill feed. The work was conducted in a very large test section and, as a result of the studies, a program was initiated that is resulting in the modernization of the entire grinding plant.

For the purpose of studying various phases of the test, it should be understood that the grinding was carried out in two stages and that the final grind was 3 to 5 per cent plus 100 mesh. It is preferable to consider the primary and secondary circuits separately (Fig. 1). Five different primary arrangements are shown, and two for the secondary circuit.

With the first or original primary circuit an 8 by 12-ft. rod mill in open circuit produced 314 tons of minus 100-mesh material per day, with a total tonnage of feed of 1238 tons. Then it will be seen how in each successive test the total tonnage of feed to the mill has been raised until finally the 8 by 12-ft. unit received a total tonnage of 11,117 tons per 24 hr. The mesh production for each of the tests shows the result of feeding the mill material on which it can work. It seems advisable to mention that in the final primary arrangement whenever the sand load in the classifier rose as high as 11,000 tons, thereby giving a total mill feed of 12,117 tons, the mill had difficulty in handling the load, and choked. It is apparent therefore that with the total tonnage of 12,117 tons, the flow capacity of the mill has been reached.

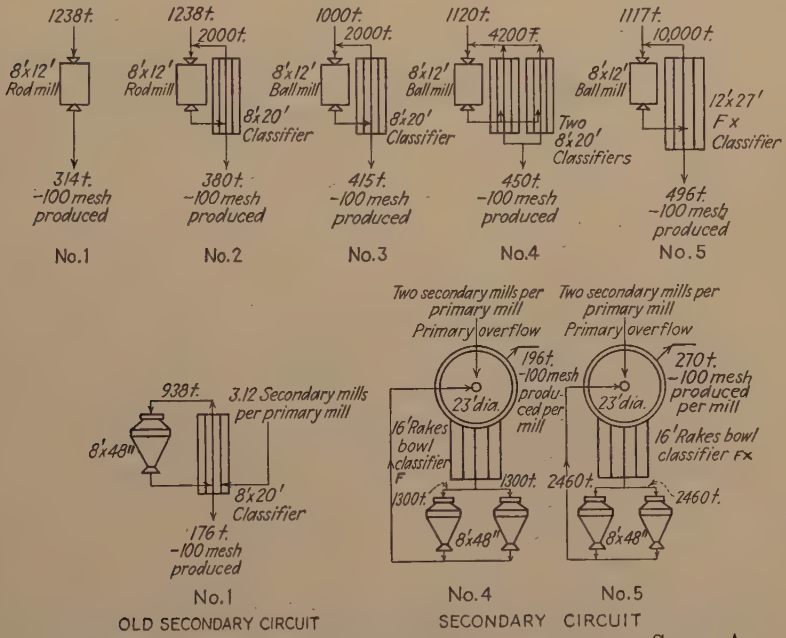


Fig. 1.—Progressive betterment by flowsheet changes at a South American mill.

In the secondary circuit, which is fed by the primary circuit, the remodeling program consisted of replacing small classifiers in closed circuit with each mill with bowl classifiers having large raking capacity, each bowl classifier being in circuit with two secondary mills. With the old secondary circuit, the ball mill with 938 tons of total feed produced but 176 tons of minus 100 mesh. This same ball mill later ground 196 tons to minus 100-mesh with 1300 tons of total feed, and, finally, with 2400 tons of total feed, produced 270 tons of minus 100-mesh. Such a demonstration brings out the fact that with adequate total tonnage of of feed, even though the circulating-load ratio is low, the mill completes a great deal of grinding by virtue of having ample feed on which to work.

### *Test in American Mill*

On a recent test in an American mill, a series of tests was run with a heavy-duty Dorr classifier and a small ball mill. The objective was to determine how much improvement in grinding could be obtained by providing classification equipment capable of carrying the sand load to higher levels than then carried. In Fig. 2 the arrangement set up for these investigations is shown in flowsheet form. The aim was to maintain a tonnage of original or new feed of about 1600 tons per day, a classifier overflow not exceeding 4 or 5 per cent on 20 mesh, and as great a tonnage through 100 mesh as possible under these conditions. By building up the classifier sand load, the total tonnage of ball-mill feed was increased. Screen analyses were made throughout the test to determine the resulting increase in grinding as measured by the additional tonnages of various meshes produced.

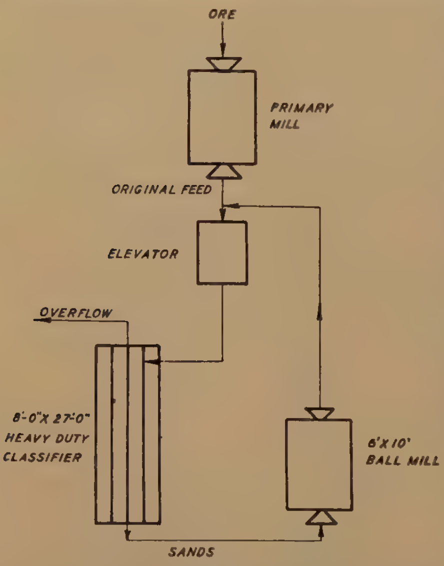


Fig. 2.—Flowsheet at an American mill.

The circuit was first operated with a moderate sand load, which, with a fixed tonnage of original feed, gave a limited amount of total ball-mill feed. The classifier sand load, and thereby the total tonnage of ball-mill feed, was then built up until a very heavy load was reached. When considered by what is believed to be a faulty measuring stick, the range of circulating-load ratio was from 2.0:1 to 4.6:1. Nevertheless, it is shown that with the low ratios of 2.0:1 and 4.6:1, an enormous tonnage of feed was carried through the grinding mill. At each stage of the program the entire circuit was sampled and screen analyses made so that the production of materials on the different meshes could be calculated and used as a basis for determining the increased grinding secured. Table 1 shows the data compiled over a long period of time, and when the circuit was operated at its upper and lower limits.

Attention is directed to the low circulating-load ratios, but at the same time the large tonnage of total feed and the mesh tons produced, which show the increased grinding obtained under the second set of conditions. If the total tonnage of feed is not considered, one is left wondering why there is such an increase in mesh production.

Experimental runs were made over a period of many days and weeks, holding the new or original feed tonnage to the circuit between 1450 and 1600 tons per day, maintaining the overflow at between 1.5 and 4.0 per cent plus 20-mesh. The percentage of solids was regulated between 35 and 45, so as to control the classifier rake product. The sand tonnage was carried between 3000 and 7000 tons per day, so as to vary the total tons of feed going to the grinding unit. Even with this high tonnage of sands, and by the same score high tonnage of total mill feed for a small ball mill, the circulating-load ratio ranged only from 2:0 to 5:1, which of course means a very moderate ratio of circulation.

TABLE 1.—*Summary of Data*

| | Lower Limit | Upper Limit |
|---|---|---|
| New feed, tons | 1585 | 1475 |
| Classifier sands, tons | 3180 | 6750 |
| Total ball-mill feed, tons | 4765 | 8225 |
| Circulating-load ratio | 2.0 | 4.6 |
| Classifier overflow, per cent: | | |
| Plus 20 mesh | 2.4 | 1.3 |
| Plus 35 mesh | 16.8 | 9.0 |
| Plus 48 mesh | 26.4 | 16.1 |
| Plus 100 mesh | 46.9 | 34.3 |
| Plus 150 mesh | 50.5 | 39.3 |
| Plus 200 mesh | 61.2 | 50.3 |
| Minus 200 mesh | 38.8 | 49.7 |
| Solids, per cent | 43.2 | 41.5 |

| Mesh | Lower Limit | Upper Limit | Net Gain |
|---|---|---|---|
| Mesh tons produced: | | | |
| 20 | 417 | 450 | 33 |
| 35 | 435 | 555 | 120 |
| 48 | 385 | 443 | 58 |
| 100 | 265 | 442 | 177 |
| 150 | 258 | 415 | 157 |
| 200 | 196 | 338 | 142 |

Fig. 3 is a graph in which results obtained have been plotted. It clearly describes how each successive increase in the classifier sand load and, as a direct result of this, increase of total tons of feed to the ball mill, was accompanied by a splendid increase of mesh production in the various meshes, especially the 100-mesh, as was desired. The 20-mesh curve is erratic, because with such a small amount of plus 20 sizes it was difficult to plot accurately.

## MECHANICAL REQUIREMENTS FOR HANDLING HEAVY TONNAGE

By actual experience it has been learned that where a high total tonnage of mill feed is to be handled, care should be taken to ensure the proper arrangement. A few points of importance are listed:

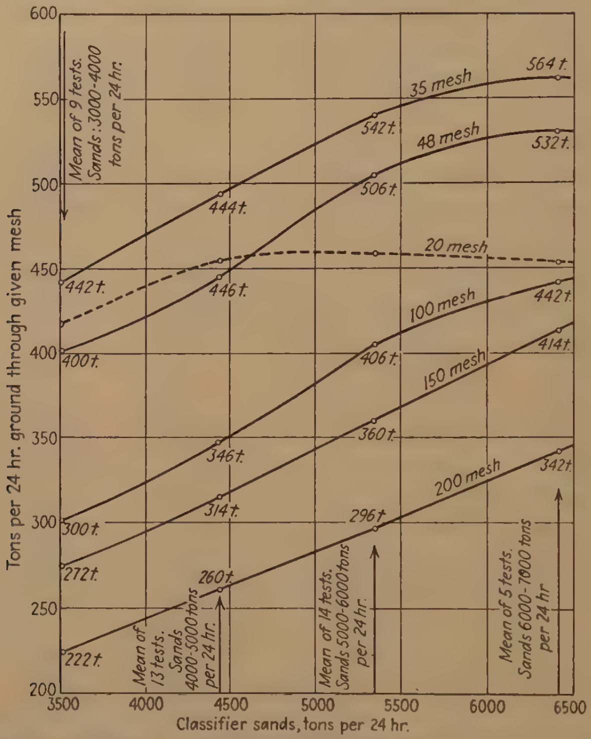


FIG. 3.—MESH-TONS GROUND WITH CONSTANT NEW FEED AND VARIABLE CIRCULATING SAND LOAD.

1. The ball mill should be relatively large in diameter and a reasonable length. The feed and outlet openings should be large, so as to accommodate the heavy flow of total feed.

2. The mill-feed scoop should have the proper spirals and be arranged with two pickups, so as to create balance. The pickup openings should be large and scoop lips should be so attached that they dig, rather than drag like a brake shoe.

3. The classifier should be designed large enough to carry adequate sand load and, at the same time, so constructed that it will remove the settled particles in a systematic manner. The classifier tank should also be placed on a proper slope for the particular conditions required.

4. A meter should be installed with the ball-mill motor, and where the operator can see it so as to show when the mill is loaded to capacity. With this meter an overload or underload is easily observed.

5. A constant-head tank for make-up water should be used, so as to ensure a constant amount of water going to the classifier.

6. Good launders should be made, so as to accommodate the large flow of coarse granular sands and mill discharge. Launder slopes are particularly important and rubber lining has been found to be very beneficial. Without such launders, the work will be a failure.

7. Classifiers may usually be installed so as to give a gravity closed circuit; i.e., mill discharge flows by gravity to the classifier and classifier sands by gravity to the mill.

8. A ball retarding grid should be used in the center discharge mill, so as to prevent steel from being carried out by the velocity of the pulp flow.

## Summary

1. Closed-circuit grinding is discussed from the standpoint of proper ball-mill pulp flow rather than circulating-load ratio.

2. Ball mills have been loaded to as high as 30 tons per cubic foot effective volume per day, with marked increase of efficiency. Several very large plants have now replaced older classifier models with heavy-duty machines, so as to carry out the actual loading of ball mills. As a direct result of this, grinding costs have been decreased and tonnages increased without additional floor space.

3. The question is raised here regarding the final outcome of crowding mill tonnage. Thus far the only limitations are mechanical. Recently a large Canadian cyanide plant conducted a series of valuable tests with a heavy-duty classifier and special ball mill. These data, which deal with the handling of a large tonnage of total ball-mill feed, will be published. This information should be of great value to the industry.

## Acknowledgment

Acknowledgment is gratefully made to the many large companies that have cooperated in carrying out such extensive work as has been done in the last few years on the subject of classification and grinding. Acknowledgment is also made to members of the Dorr Company staff for valuable suggestions offered when the handling of large circuits presented trying problems.

# Use of the Coercimeter in Grinding Tests

By Fred D. DeVaney* and Will H. Coghill,* Members A.I.M.E.

(New York Meeting, February, 1938)

The coercimeter, as its name implies, is an instrument for measuring the coercive force† of magnetic substances. It was developed by Davis and Hartenheim in the Special Studies Section, Metallurgical Division. A detailed description of this apparatus may be found elsewhere.[2]

The coercive force determinations of magnetic materials are interesting because of the relationship established by Gottschalk,[4] who showed a linear relationship between the magnetization coercive force and the specific surface of comminuted particles.

The value of this relationship in determining grinding efficiency has been shown by Dean.[3] The determination of the surface contained in the subsieve sizes has always been a difficult problem for investigators. They made approximate measurements of the surface of coarse materials by sizing on screens, but for the determination of the surface of the subsieve sizes it was necessary to make detailed grain counts or elutriation tests, or to study dissolution rates. The technical literature contains many references to other methods for determining these surfaces, either by some special apparatus or by mathematical calculations based on distribution lines. Many of the methods are long and tedious, and the results of some, at least, are questionable. The turbidimeter gives quick results on ground cement.

By using magnetite as the material to be ground, a simple determination of its coercive force by the coercimeter, requiring 10 minutes or less, can be transposed directly and accurately into units of relative surface. This subject has been pursued further by the U. S. Bureau of Mines in cooperation with the Missouri School of Mines and Metallurgy, Rolla, Mo., and the following is a description of the results.

---

Published by permission of the Director, U. S. Bureau of Mines. This paper represents the results of cooperative work between the Bureau of Mines, U. S. Department of the Interior, and the Missouri School of Mines and Metallurgy, Rolla, Mo. Manuscript received at the office of the Institute June 30, 1937. Issued as T.P. 862 in Mining Technology, January, 1938.

* Associate Metallurgist and Supervising Engineer, respectively, Ore Dressing Section, Metallurgical Division, U. S. Bureau of Mines, Rolla, Mo.

† Coercive force is the demagnetizing force necessary to remove the residual magnetism of a magnetized substance. It is the tenacity with which magnetism is retained. When this force is low, the substance loses its magnetism rapidly.

[2] References are at the end of the paper.

## The Coercimeter

The underlying principle of the coercimeter (Fig. 1) is simple. A sample of magnetic material is magnetically saturated by placing it in a strong electromagnetic field. It is then removed to a controlled magnetic field, where a balance between the controlled magnetic field and the magnetic field of the sample is obtained. The reading of the controlled magnetic field or demagnetizing force is in amperes. It gives a measure of the magnetization-coercive ($H_c$) force.

To determine the coercive force of a granular sample, the material is packed tightly by tapping in a brass capsule, which has a screw top, so that the grains are held in place and will not move under the action of a magnetic field. The sample in the capsule is magnetically saturated by placing it between the pole pieces of the strong electromagnet *A* for about 5 seconds. After magnetization, the capsule is placed in holder *B* and inserted to the mid-point of the long primary solenoid *C*. By means of resistances *D*, the field of the primary coil is balanced against the field of the magnetized specimen. This balance is obtained by varying the current to the primary coil, so that when the secondary coil *E*, which is mounted on wheels and runs on a miniature track, is given a sudden push there will be no deflection of the needle of the galvanometer *F* connected to the secondary coil. The demagnetizing current, or current to the primary solenoid, is measured by ammeter *G*. The coercive force of the substance expressed in oersteds ($H_c$) can be calculated directly by multiplying the reading, in amperes, by an instrument constant which, with the present instrument, is 22.97. Check readings by different workers can be made with remarkable accuracy. When many determinations are required, an extra capsule may be provided so that one operator may do the loading while a companion manipulates the instrument.

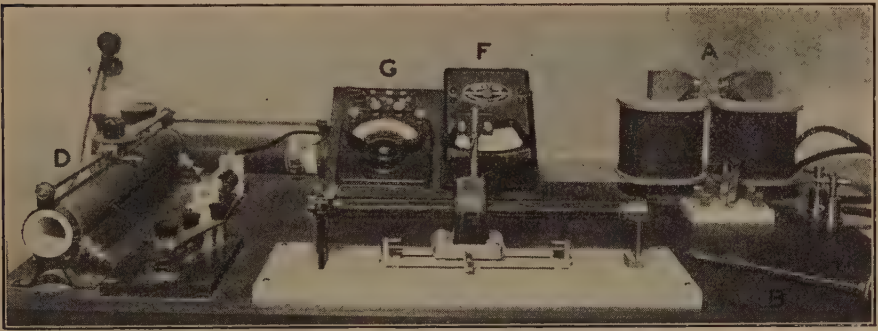


Fig. 1.—Model 2 coercimeter.

## Material Used in Investigation

As pointed out by Dean,[3] magnetite is almost an ideal substance for the study of grinding. It can be obtained relatively pure and at reasonable cost, and its grindability is about the same as that of the average ore. On account of the wide spread in the coercive-force values of coarse and fine sizes, a significant value for the amount of surface in any ground sample can be determined readily. Since magnetite is a mineral in exactly the same sense as quartz or calcite, it is evident that any fundamental laws of grinding found to hold for magnetite will likewise hold for any other mineral when the difference in grindability is considered.

Three thousand pounds of sized high-grade magnetite concentrates from the Old Bed seam of the Witherbee Sherman Corporation at Mineville, N. Y., were secured. This material had a tenor of 66.7 per cent of iron, 4.5 per cent of silica, and 0.174 per cent of phosphorus, and had the sizing analysis shown in Table 4.

## Relation between Particle Size, Specific Surface, and Coercive Force

To determine the relationship of particle size to coercive force, a sample was reduced further, so that only a small amount remained on 10 mesh. Any nonmagnetic material liberated by crushing was removed by magnetic concentration. The cleaned material, having a tenor of 69.41 per cent of iron and 1.14 per cent of silica, was then demagnetized and screened down to 400 mesh. Material finer than this could not be sized hydraulically because of the floccules induced by residual magnetism. It was, however, fractionated pneumatically in the air separator through the courtesy of Dr. Roller.[6] The sized increments were washed to remove adhering dust particles. The mean particle diameters of the sized products were determined by the filar micrometer and are recorded in Table 1, with their respective sieve sizes. Dr. C. E. Brown, chemist at the Health Division of the U. S. Bureau of Mines, assisted in the measurement of some of the finest sizes by using the microprojector. Incidentally, all the mean diameters seem abnormally large when compared with the mesh of the sieves, but this has no relation to the problem. Other researchers[5] have investigated and accepted this abnormality.

The relationship between mean particle diameter, specific surface and coercive force will be seen in Table 1, and the straight-line relationship of the last two are shown in Fig. 2. When it is required to reduce coercive force to reciprocal microns, Fig. 2 or the formula shown in Table 1 may be used. Values for the coercive force of particles finer than 10 microns are not shown, as the present instrument is not designed to measure coercive force with values of more than 100 oersteds. This, however, was no detriment in the grinding study, because the finest mixtures had a coercive value not greater than 45 oersteds.

TABLE 1.—*Relation between Particle Size, Specific Surface, and Coercive Force of Mineville Magnetite*

| Size | Mean Particle Diameter, Microns | Specific Surface Reciprocal, Microns | Coercive Force ($H_c$), Oersteds |
|---|---|---|---|
| Mesh | | | |
| +10 | 2,950 | 0.00034 | 16.76 |
| 14 | 2,020 | 0.00049 | 16.76 |
| 20 | 1,435 | 0.00069 | 16.76 |
| 28 | 1,018 | 0.00098 | 16.76 |
| 35 | 720 | 0.00139 | 16.76 |
| 48 | 510 | 0.00196 | 17.23 |
| 65 | 359 | 0.00279 | 17.68 |
| 100 | 254 | 0.00393 | 19.63 |
| 150 | 193 | 0.00518 | 20.67 |
| 200 | 127 | 0.00787 | 23.20 |
| 270 | 106 | 0.00943 | 24.35 |
| 400 | 70.7 | 0.0141 | 27.56 |
| −400 mesh + 20 microns......... | 29.3 | 0.0341 | 45.02 |
| −20 + 10 microns.............. | 14.43 | 0.0693 | 72.58 |

The empirical formula for coercive force of Mineville magnetite is:

$$H_c = 820\left(\frac{1}{d}\right) + 15.9$$

No difference appears in the coercive force of the sized increments between 10 and 35 mesh, because Mineville magnetite is made up of grains ranging from 48 to 100 mesh. Since the coercimeter gives a measure of the outside surface of the particle as well as of the unexposed grain surfaces, only by the crushing of unit grains is new surface made and the coercive force increased.

At first thought it might seem that this fact would make impossible the use of finely crystalline magnetite in grinding studies, but the facts are that for the most gentle grinding the amount of new surface represented by a change of percentage on the coarser screens is almost negligible, compared with the activity of subsieve material; as much surface is presented by 0.1 per cent of minus 200-mesh material as by 10 per cent of 10-mesh material. A coarser-grained magnetite would undoubtedly be superior, since the straight-line relation between the coercive force and the specific surface, as shown by Fig. 2, would hold for coarser particles. The surface in the coarser sizes can be calculated readily, however, if this seems necessary.

## Effect of Dilution on Coercive Force

The magnetite used in making coercimeter tests need not be of high purity. Experiments were made with minus 100-mesh magnetite assaying 71.65 per cent iron and 0.20 per cent silica, diluted with varying amounts of ground silica. The coercive force of the various mixtures was determined. The results are given in Fig. 3, which shows that an admixture of 10 per cent silica reduced the coercive force only 1.5 per cent and the admixture of 50 per cent reduced the coercive force only 5 per cent.

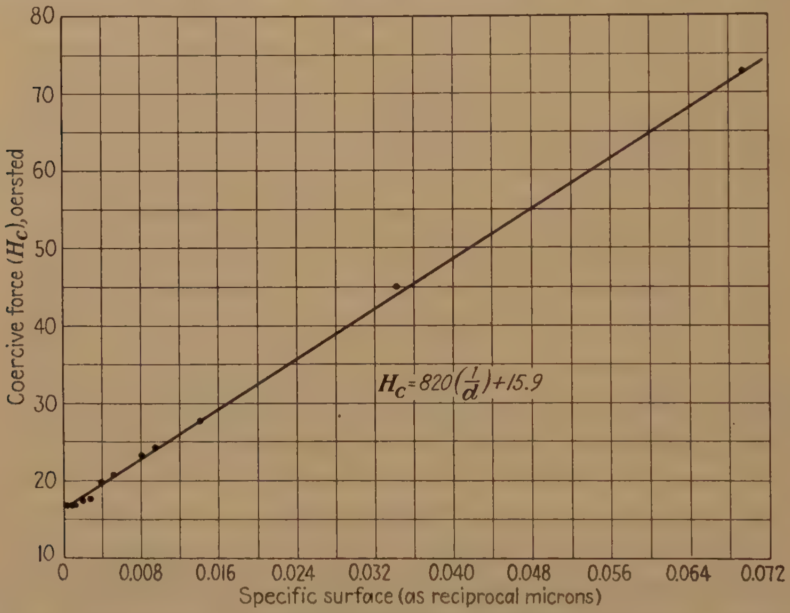


Fig. 2.—Variation of coercive force with specific surface. Mineville magnetite.

## Relation of Work Input to Coercive Force

Dean[3] has presented data to prove that there is a clear-cut linear relationship between work input and coercive force. There is also direct proportional relationship between work input and new or increased coercive force. These data tended to establish more firmly Rittinger's law of grinding. The work reported by Dean was on Ural Mountains magnetite in definite coarse octahedra. Inasmuch as the material available for the present crushing studies (Mineville magnetite) was more finely crystalline and was thought to differ in grindability from the Ural Mountains material, a similar experiment was made. The frictionless drop-weight device was used for crushing, and the coercimeter was used for measuring the surface produced. The results are in Table 2 and Fig. 4.

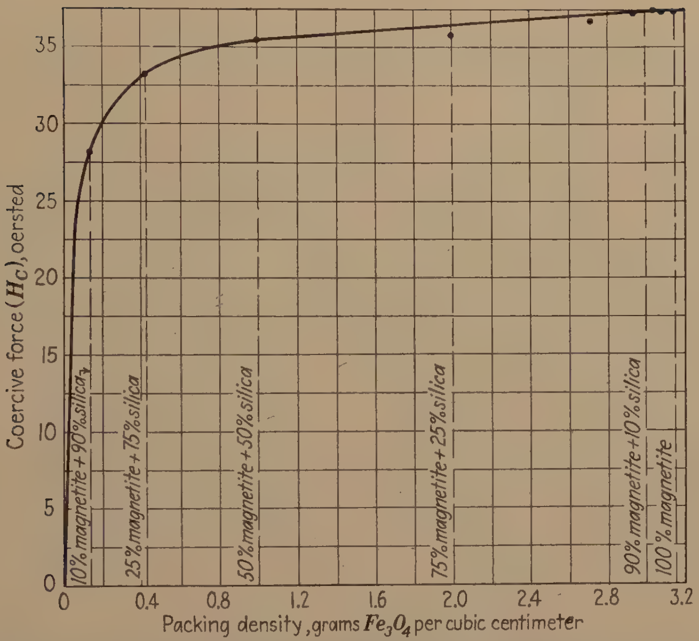


FIG. 3—VARIATION BETWEEN PACKING DENSITY AND COERCIVE FORCE.

Minus 100 plus 150-mesh Mineville magnetite diluted with various amounts of silica.

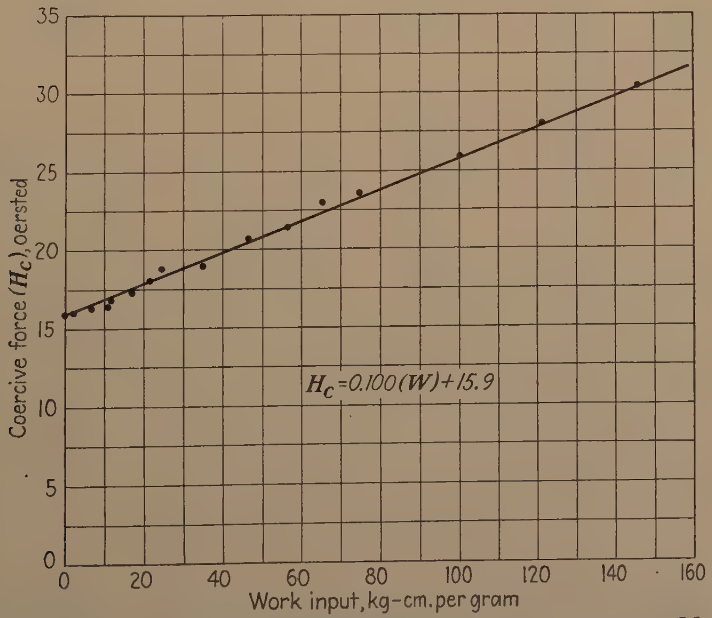


FIG. 4.—RELATION OF COERCIVE FORCE TO WORK INPUT IN GRINDING MINEVILLE MAGNETITE.

The coercive force of the ground Mineville magnetite was also found to bear a linear relationship to the work input, which can be expressed by the following equation

$$H_c = 0.100W + 15.9$$

where $W$ is expressed in kilogram-centimeters per gram. The grindability of the Mineville magnetite was of the same order as the Ural Mountains sample ($H_c = 0.093W + 5.2$). Owing to the higher massive constant for the former material (15.9), as compared with 5.12 for the Ural Mountains magnetite, the coercive force values for the Mineville magnetite were considerably higher.

For the sake of the present problem, it is assumed that the drop-weight device gives a true measure of the work done in grinding. Since we have established the work required to produce a specified amount of new surface for Mineville magnetite, we may use this material for grinding tests with other types of machines, measure the power input, the resulting surface by the coercimeter, and determine the relative grinding efficiency of the machine tested.

Table 2.—*Relation of Coercive Force and Work Input for Crushing Mineville Magnetite*

| Sample | Coercive Force, Oersteds | Work Input, Kg-cm. per Gram | Sample | Coercive Force, Oersteds | Work Input, Kg-cm. per Gram |
|---|---|---|---|---|---|
| 1 (heads) | 15.9 | | 9 | 19.1 | 34.8 |
| 2 | 16.1 | 2.2 | 10 | 20.7 | 46.3 |
| 3 | 16.3 | 6.5 | 11 | 21.5 | 56.5 |
| 4 | 16.5 | 10.9 | 12 | 23.0 | 65.2 |
| 5 | 16.8 | 11.9 | 13 | 23.7 | 74.4 |
| 6 | 17.1 | 17.4 | 14 | 25.9 | 100.2 |
| 7 | 18.1 | 21.2 | 15 | 28.0 | 121.3 |
| 8 | 18.8 | 24.4 | 16 | 30.3 | 145.4 |

## Comparison of Useful and Ultimate Grinding

*In Different Circulating Loads.*—In ore milling, the mill operator usually measures the capacity of his grinding unit in tons of material ground to the desired size, or speaks of the efficiency of his mill in terms of tons per horse-power-hour ground through a limiting screen. These terms give the shortest approach to useful grinding. For a good diagnosis, however, the method has to be more extensive.

Whereas the coercimeter may be used to determine ultimate grinding, the reciprocal values that stand in juxtaposition with coercive force may be used for useful grinding. In using the reciprocals for useful grinding, the reciprocal next below the limiting sieve is applied to the whole amount passing that screen. This method introduces values comparable with and of the same denomination as those for ultimate grinding. A ratio between useful and ultimate grinding may then be found. In the experiments to be discussed, useful grinding was considered as stopping at 200 mesh, and all material finer than this was considered as being minus 200 plus 270-mesh in size.

By way of illustrating the use of the coercimeter and to determine the relation of useful to ultimate grinding in a ball mill with circulating loads differing in magnitude, a series of eight closed-circuit tests is shown. In these tests the circulating load varied from 24 to 294 per cent. The material was finished at 65 mesh and the coercimeter was used to find relative surface of the finished material. These tests, given in Table 3, show how much the useful and ultimate grinding increased with an increase in circulating load. They show that the average particle size of the finished material became coarser with increased circulating load and that the relative amount of useful to ultimate grinding increased with the circulating load.

TABLE 3.—*Comparison of Useful and Ultimate Grinding with Various Circulating Loads*

MINEVILLE MAGNETITE FINISHED AT 65 MESH IN CLOSED-CIRCUIT DRY GRINDING

| Length of Cycles, Minutes | Circulating Load, Per Cent | Finished Product | | | | Grinding | | | Relation of Useful to Ultimate Grinding, Per Cent |
|---|---|---|---|---|---|---|---|---|---|
| | | Coercive Force, Oersteds | Average Particle Size, Microns | Specific Surface as Reciprocal Microns | | Output per Minute, −65 Mesh, Grams | Useful, Grams × Useful Specific Surface | Ultimate, Grams × Ultimate Specific Surface | |
| | | | | Useful | Ultimate | | | | |
| 20 | 24 | 35.7 | 41.5 | 0.0080[a] | 0.0241[a] | 80.0 | 0.608 | 1.895 | 32.2 |
| 16 | 43 | 35.4 | 42.0 | 0.0077 | 0.0238 | 87.2 | 0.636 | 2.042 | 31.2 |
| 14 | 53 | 34.3 | 44.4 | 0.0076 | 0.0225 | 93.6 | 0.673 | 2.068 | 32.6 |
| 12 | 67 | 34.2 | 44.8 | 0.0076 | 0.0223 | 99.7 | 0.718 | 2.185 | 32.9 |
| 10 | 92 | 33.5 | 46.5 | 0.0075 | 0.0215 | 104.0 | 0.738 | 2.195 | 33.6 |
| 8 | 126 | 32.1 | 50.5 | 0.0073 | 0.0198 | 110.3 | 0.762 | 2.140 | 35.6 |
| 6 | 189 | 31.6 | 51.5 | 0.0072 | 0.0194 | 116.0 | 0.789 | 2.204 | 35.8 |
| 4 | 294 | 31.0 | 54.3 | 0.0070 | 0.0184 | 122.9 | 0.811 | 2.215 | 36.6 |

[a] For net specific surface deduct 0.00043, the specific surface of the feed.

With increased circulating load the output increased 54 per cent, the useful surface increased 33 per cent, and the ultimate grinding (ultimate new surface) increased 17 per cent. This illustrates that in the grinding of coal, where surface is the important factor, a heavy circulating load is not as important as in the grinding of ores.

If ultimate surface is of prime consideration, the gain by pressing the circulating load is not great. In the grinding of coal and cement clinker, although the application of circulating loads should not be discouraged, the gain is not as great as in ore milling, where liberation of the mineral particles is the first consideration.

*With Different Ball Sizes.*—Table 4 shows the results of two pairs of tests in which Mineville magnetite was ground with 2-in. and with ⅝-in. balls. In each pair of tests the grinding period was timed so that the amounts of minus 200-mesh material were nearly the same. The pairs of tests differed in severity of grind; in one pair about 29 per cent, and in the other pair about 10 per cent, of minus 200-mesh material was made.

TABLE 4.—*Effect of Different Ball Sizes*

| Size, Mesh | Weight, Per Cent | | | | |
|---|---|---|---|---|---|
| | Feed | 2-in. Balls | ⅝-in. Balls | 2-in. Balls | ⅝-in. Balls |
| 6 | 2.8 | | 0.9 | | 1.3 |
| 8 | 26.6 | | 7.9 | | 10.9 |
| 10 | 54.4 | | 16.6 | 0.1 | 23.6 |
| 14 | 15.2 | | 14.3 | 0.9 | 18.2 |
| 20 | 0.7 | | 7.8 | 5.4 | 9.5 |
| 28 | 0.1 | 0.4 | 4.2 | 13.7 | 5.5 |
| 35 | | 3.8 | 3.3 | 18.8 | 3.9 |
| 48 | | 12.7 | 2.7 | 16.2 | 3.3 |
| 65 | 0.2 | 16.7 | 2.1 | 11.9 | 2.7 |
| 100 | | 16.7 | 3.0 | 10.1 | 3.1 |
| 150 | | 12.0 | 3.7 | 6.8 | 3.1 |
| 200 | | 8.9 | 4.6 | 4.9 | 3.1 |
| −200 | | 28.8 | 28.9 | 11.2 | 11.8 |
| | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| Grinding period, minutes | | 39 | 30 | 16 | 13 |
| Grams per minute[a] | | 51.3 | 66.7 | 125.0 | 153.7 |
| Coercive force, oersteds | 16.3 | 28.1 | 28.4 | 21.9 | 22.1 |
| Mean specific surface, reciprocal microns | 0.0004 | 0.0148 | 0.0152 | 0.0073 | 0.0076 |
| Ultimate grinding, grams per minute × new surface | | 0.738 | 0.987 | 0.863 | 1.105 |
| New useful surface, reciprocal microns | | 0.0061 | 0.0045 | 0.0036 | 0.0023 |
| Useful grinding, grams per minute × useful new surface | | 0.333 | 0.303 | 0.451 | 0.355 |
| Minus 200-mesh portion, coercive force, oersteds | | 49.3 | 58.1 | 52.8 | 59.7 |
| Relation of useful to ultimate grinding, per cent | | 45.1 | 31.4 | 52.3 | 32.2 |

[a] The mill contained 2000 grams of magnetite.

The smaller balls gave more ultimate grinding per minute. They left unfinished more of the coarser sizes, but they made up for this loss by additional grinding of the minus 200-mesh size. A jump must not be made to the conclusion that the ⅝-in. balls would be superior in closed-circuit grinding. Some of the coarse sizes might resist reduction and build up to a deleterious amount in the returning feed.

The larger balls gave more useful grinding (credit to and through 200 mesh) per unit of time, and their relation of useful to ultimate grinding was more favorable.

Several trials in closed circuit with media of a size between those indicated would have arrived at the optimum size for useful grinding and the optimum size for ultimate grinding. Here, only the procedure is outlined.

## Efficiency of Ball Mill Compared with Drop-weight Device

The coercimeter has proved to be valuable in securing data on the deportment of the drop-weight device. Variation, such as size of sample, difference in the sizes of balls, mortar and pestle, height of drop, etc., have given confusing results. Because of the small size of samples used in the drop-weight operation, comparisons on the basis of screen tests necessitated many tests to give enough material to be screened. Furthermore, the screen tests were not satisfactory, since the surface in the subsieve sizes could not be evaluated. With the coercimeter it is possible to make quickly the surface determination on small samples. This has led to a better understanding of the performance of the device. The present work is more accurate than that already reported by the writers.[1]

Raymond Wilson[7] has pointed out that, as compared with the drop-weight device (net power), the efficiency of the ball mill (gross power) in the dry grinding of cement clinker ranges from 13 to 43 per cent. He used the turbidimeter for ultimate surface. In the present paper, wet ball milling is compared with the drop-weight device. The results are given in Table 5. In the upper part of the lower section the results are in terms of useful grinding as commonly used by the present writers. (A unit of surface is assigned to a unit weight of the 1-in. size, and the reciprocals are employed in the usual manner.) There it will be seen that the surface tons per horsepower-hour for the ball mill are much lower than for the drop-weight. The same relative values would have resulted if reciprocal microns had been used.

Then, again, to illustrate and utilize the new system the results at the bottom of the table were obtained. They are based on coercive force and give ultimate grinding. In ultimate grinding the performance of the ball mill was more favorable with respect to the drop-weight than in useful grinding. A contributing factor was the extra fineness of the minus 200-mesh portion made by the ball mill. The ultimate grinding of the ball mill was 65.5 per cent of the drop-weight. This figure is higher than the 13 to 43 per cent mentioned by Wilson. The explanation that the wet ball milling practiced by the present writers is known to be more efficient than the dry method used by him suffices to account for the difference.

TABLE 5.—*Comparison of Wet Ball-mill and Dry Drop-weight Grinding*

| Size, Mesh | Weight, Per Cent | | |
|---|---|---|---|
| | Feed | Drop-weight Grinding | Ball-mill Grinding |
| 6 | 2.8 | | 0.5 |
| 8 | 26.6 | | 3.5 |
| 10 | 54.4 | | 9.9 |
| 14 | 15.2 | 2.1 | 13.7 |
| 20 | 0.7 | 12.0 | 13.9 |
| 28 | 0.1 | 13.9 | 11.8 |
| 35 | | 20.0 | 10.4 |
| 48 | | 11.7 | 8.1 |
| 65 | 0.2 | 10.9 | 7.0 |
| 100 | | 8.8 | 5.3 |
| 150 | | 6.5 | 4.3 |
| 200 | | 3.7 | 2.9 |
| −200 | | 10.4 | 8.7 |
| | 100.0 | 100.0 | 100.0 |
| New surface units (200 mesh) | | 130.7 | 97.1 |
| Surface tons per horsepower-hour | | 122.1 | 52.2 |
| Tons per horsepower-hour | | 0.934 | 0.538 |
| Coercive force, oersteds | | 19.3 | 19.7 |
| Specific surface as reciprocal microns | | 0.00415 | 0.00467 |
| Coercive force, oersteds, −200-mesh portion | | 37.9 | 44.2 |
| Specific surface as reciprocal microns, −200-mesh portion | | 0.0268 | 0.0345 |
| Ultimate grinding, specific surface × tons per horsepower-hour | | 0.00347 | 0.00228 |

$$\text{Ratio } \frac{\text{Useful grinding, ball mill}}{\text{Useful grinding, drop-weight device}} = \frac{52.2}{122.1} = 42.8 \text{ per cent}$$

$$\text{Ratio } \frac{\text{Ultimate grinding, ball mill}}{\text{Ultimate grinding, drop-weight device}} = \frac{0.00228}{0.00347} = 65.5 \text{ per cent.}$$

## COMPARISON OF LOADS OF MIXED AND OF SEGREGATED BALLS

Some novel tests were made with the coercimeter. In the first series the balls were mixed and in the second, segregation by a grid was hypothecated.

First, a charge was ground for 15 min. with a ball load of 50 per cent of 2-in. balls and 50 per cent of ¾-in. balls, and second, a charge was ground for 7½ min. with a full load of 2-in. balls, after which the balls were replaced by a full load of ¾-in. balls. The grinding was continued for 7½ min., to equal the period in the first test. The results are shown in Table 6.

Table 6.—*Dry Grinding of Mineville Magnetite with Mixed and Segregated Ball Loads*

| Size, Mesh | Weight, Per Cent | | | | |
|---|---|---|---|---|---|
| | Feed | 2-in. and ¾-in. Balls | 2-in. Balls | ¾-in. Balls[a] | |
| 6 | 2.8 | | | | |
| 8 | 26.6 | 0.3 | 0.1 | | |
| 10 | 54.4 | 0.4 | 0.5 | 0.4 | |
| 14 | 15.2 | 0.9 | 2.5 | 1.1 | |
| 20 | 0.7 | 1.4 | 8.3 | 2.3 | |
| 28 | 0.1 | 2.0 | 14.1 | 3.0 | |
| 35 | | 6.0 | 16.6 | 7.6 | |
| 48 | | 10.7 | 14.6 | 10.8 | |
| 65 | 0.2 | 13.6 | 10.9 | 13.0 | |
| 100 | | 15.7 | 9.8 | 15.1 | |
| 150 | | 12.0 | 6.4 | 11.8 | |
| 200 | | 9.3 | 4.1 | 8.4 | |
| −200 | | 27.7 | 12.1 | 26.5 | |
| | 100.0 | 100.0 | 100.0 | 100.0 | |

| | | | | | Over-all |
|---|---|---|---|---|---|
| Surface tons per hour | | 37.6 | 42.6 | 29.6 | 36.1 |
| Surface tons per horsepower-hour | | 34.1 | 39.4 | 27.5 | 33.5 |
| Tons per hour | | 0.15 | 0.30 | 0.30 | 0.15 |
| Horsepower | | 1.10 | 1.08 | 1.08 | 1.08 |
| Tons per horsepower-hour | | 0.136 | 0.278 | 0.278 | 0.139 |
| Time, min | | 15 | 7.5 | 7.5 | 15 |
| Coercive force, oersteds | 16.3 | 27.1 | 21.5 | 27.7 | 27.7 |
| Mean specific surface as reciprocal microns | 0.00043 | 0.0132 | 0.0066 | 0.0139 | 0.0139 |
| Coercive force of minus 200-mesh | | 47.6 | 49.3 | 49.3 | 49.3 |
| Mean specific surface of minus 200-mesh | | 0.0372 | 0.0393 | 0.0393 | 0.0393 |
| Ball mill ultimate grinding, surface (1/*d*) tons per hp-hr | | 0.0018 | 0.0018 | 0.0020 | 0.0019 |

[a] Feed consisted of ground material from previous test with 2-in. balls.

The ultimate evaluations by the old method and by the new method employing the coercimeter are so nearly identical that the manner of evaluating needs no comment. There is, however, one pair of values that at first glance may impress the student of principles of grinding as inconsistent. In the series simulating the grid, the mean specific surfaces of the 200-mesh products are all the same; that is, 0.0393. This seems illogical when the percentage weight is considered; if the ball sizes had not been changed, the 12.1 per cent weight product would be expected to be coarser than its companion, 26.5 per cent. However, the observed identity is not strange because the ball sizes used are different. In some work not published, balls that are too big have been shown to do nonselective grinding as vigorously as balls that are too small. Hence there is no discord.

The results of these tests provoke a consideration of principles that must not be passed lightly. What if the first test had been made with one size of balls, all of which had the average weight of those in the mixture? The ball of average weight would have had a diameter of 0.93-in. Again, what if the test had been made with one size of balls, all of which had the average surface of those in the mixture? The ball of average surface would have had a diameter of 0.86 in. This question does not interest the operator and has not been pursued exhaustively, but the tests that have been made indicate that balls of a single size, 1 in. in diameter or smaller, would have given identical results.

## Some Uses of the Coercimeter in Principles of Grinding

Certain definite and advantageous uses of the coercimeter have been sketched for studying the principles of grinding when clean magnetite is employed. Interested observers have wondered if the use could not be extended to other ores by admixing a small amount of magnetite, magnetically separating it from the ore after the grind, and then following the procedure already outlined. The answer is that if the grindability of an ore is sought, substitutions cannot be made. If different machines are to be compared, the differential grinding in the mixture would defeat the objective. It is enough that by using magnetite the coercimeter can be employed as one of the greatest boons ever introduced in the study of grinding.

## References

1. W. H. Coghill and F. D. DeVaney: Conducting Grinding Tests for Easy Interpretation of Results. U. S. Bur. Mines *R.I.* 3239 (1934) 5.
2. C. W. Davis and M. Hartenheim: A Simple Method for the Determination of Magnetization by Coercive Force. *Rev. Sci. Instruments* (1935) **7**, 147–149.
3. R. S. Dean: Magnetite as a Standard Material for Measuring Grinding Efficiency. Page 324, this volume.
4. V. H. Gottschalk: Coercive Force of Magnetite Powders. U. S. Bur. Mines *R.I.* 3268 (1935) 83–90; also *Physics* (1935) **6**, 127–132.
5. V. H. Gottschalk and F. S. Wartman: Magnetization Curves for Magnetite Powders. U. S. Bur. Mines *R.I.* 3268 (1935) 68.
6. P. S. Roller: Separation and Size Distribution of Microscopic Particles—An Air Analyzer for Fine Powders. U. S. Bur. Mines *Tech. Paper* 490 (1931).
7. R. Wilson: Method of Estimating the Efficiency of Pulverizers. A.I.M.E. *Tech. Pub.* 810 (1937), 12.

# DISCUSSION

(*T. B. Counselman presiding*)

E. W. Davis,* Minneapolis, Minn.—In 1915 we studied the effect of changing the size of balls, and found, to our surprise, that a very small change in the average diameters of the balls had a radical effect on the size of the circulating load when grinding the same tonnage to the same classifier overflow size. Going further, we found, to our satisfaction at least, that using balls that were all approximately the same size gave the smallest circulating load, all of which indicated that the small balls should be removed from the mill. I believe it is a practice now at some plants to remove the small balls occasionally, but at most plants the difficulty of removing them is so great that the gain in grinding efficiency may not be worth the trouble. I am very glad to see that detailed studies of ball charges are being made. This subject seems to have been somewhat neglected.

---

* Superintendent, Mines Experiment Station, University of Minnesota.

# Grindability and Grinding Characteristics of Ores

By Fred C. Bond* and Walter L. Maxson,† Members A.I.M.E.

(New York Meeting, February, 1938)

This paper is a continuation of two earlier papers,[1,2] and presents new data on the grindability of various ores and other materials—the results of several years of intermittent research work on the nature of grinding and interpretation of test results. It is divided into five parts:

1. The tabulated results of several hundred grindability tests on a wide variety of ores.
2. A method of correcting screen analyses and calculating from them the surface and other properties.
3. A description of a new method of measuring the "surface energy" of an ore by pendulum impact tests.
4. Test results.
5. A general discussion of the test results and their application to grinding problems.

## 1. GRINDABILITY OF VARIOUS ORES

This part is a continuation of the paper listed as reference No. 1. The method of testing is described in detail in that paper. The sample to be tested is crushed to all through 6 mesh in rolls set at 1/16-in. opening in closed circuit with a screen. Of this sample 700 c.c. is ground dry in a laboratory ball mill under constant conditions of mill speed and ball charge in closed circuit with a screen of the desired size at 250 per cent circulating load. The mill is cylindrical, 12 by 12 in., and rotates at 70 r.p.m. It contains a charge of 285 iron balls weighing 20,125 grams and ranging from 1½ to ¾ in. in diameter. Each test is continued for a sufficient number of periods to establish equilibrium at 250 per cent circulating load, or until the composition of the circulating load is constant for successive periods.

Tests are conducted at the mesh size to which the ore is to be ground in practice, and the results are expressed as the net production in grams of screen undersize per revolution of the mill. This is designated as the

---

Manuscript received at the office of the Institute Dec. 1, 1937. Issued as T.P. 888 in Mining Technology, March, 1938.

* Allis-Chalmers Mfg. Co., West Allis, Wis.

† Allis-Chalmers Mfg. Co., Milwaukee, Wis.

[1] References are at the end of the paper.

### TABLE 1.—*Summary of Tests*

| Ore | Description | Location | Net Grams per Revolution | | −200 Mesh in Product, Per Cent | Specific Gravity | |
|---|---|---|---|---|---|---|---|
| | | | | | | Apparent | True |
| TESTS AT MINUS 28 MESH | | | −28 Mesh | −200 Mesh | | | |
| Gold | Bernheim | S. Rhodesia | 1.26 | 0.374 | 27.9 | 1.77 | |
| Gold | Wright Hargreaves | Ontario | 1.338 | 0.483 | 34.2 | 1.70 | 2.68 |
| Gravel | Pacific Coast aggregates | California | 1.58 | 0.398 | 25.2 | 1.53 | |
| Gold | Portland | Colorado | 1,966 | 0.551 | 27.2 | 1.63 | 2.69 |
| Copper | New Cornelia | Arizona | 2.50 | 0.708 | 30.4 | 1.63 | 2.68 |
| Gold | Little Long Lac | Ontario | 2.726 | 1.166 | 40.2 | 1.69 | 2.64 |
| Gold | San Luis | Mexico | 2,905 | 0.552 | 20.5 | 1.67 | |
| Gold | Benguet | Philippine Islands | 3.12 | 0.833 | 31.4 | 1.69 | 2.66 |
| Gold | East Rand | S. Africa | 3.22 | 0.616 | 22.9 | 1.78 | 2.71 |
| Copper | Miami Copper Co. | Arizona | 3.37 | 0.906 | 26.9 | 1.64 | 2.69 |
| Quartz | Canada silica products | Canada | 3.58 | 0.413 | 11.7 | 1.56 | |
| Gold | Homestake | S. Dakota | 3.95 | 1.318 | 35.5 | 1.91 | 3.12 |
| Dwight-Lloyd sinter | Eagle Picher | Illinois | 4.01 | 0.842 | 21.1 | 2.25 | |
| Silver | Hualgayoc | Peru | 4.27 | 1.020 | 25.2 | 2.45 | |
| Quartz | Pure crystallized | California | 4.55 | 0.739 | 17.0 | 1.68 | 2.65 |
| Cassiterite | Vulcan detinning | New Jersey | 5.09 | 1.115 | 23.1 | 3.60 | |
| Syenite | Canadian nepheline syenite | Ontario | 5.51 | 0.743 | 16.7 | 1.63 | 2.73 |
| Phosphate | Charleston Min. Co. | Tennes ee | 8.87 | 1.070 | 14.3 | 1.86 | |
| Gold | Red Cross Min. Co. | California | 20.90 | 4.390 | 26.7 | 1.57 | |
| TESTS AT MINUS 35 MESH | | | −35 Mesh | −200 Mesh | | | |
| Iron borings | Du Pont | Delaware | 0.061 | 0.00648 | 8.6 | 3.14 | |
| Cast iron | Crucible Steel | Pennsylvania | 0.611 | 1.59 | 2.6 | 0.95 | |
| Copper | Phelps Dodge | Arizona | 2.310 | 0.736 | 34.7 | 1.63 | 2.68 |
| Gold | Little Long Lac | Ontario | 2.350 | 0.681 | 32.6 | 1.69 | 2.64 |
| Gold | Benquet Cons. | Philippine Islands | 2.380 | 0.728 | 35.6 | 1.69 | 2.66 |
| Gold | East Rand | S. Africa | 2.404 | 0.576 | 27.7 | 1.78 | 2.71 |
| Gold | San Luis | Mexico | 2.495 | 0.603 | 25.7 | 1.67 | |
| Iron | Bowring-Keradid | Morocco | 2.970 | 0.742 | 25.0 | 1.86 | |
| Iron | Bowring-Belmonte | Morocco | 3.03 | 0.627 | 20.9 | 2.12 | |
| TESTS AT MINUS 48 MESH | | | −48 Mesh | −200 Mesh | | | |
| Coke | Aluminum Co. of America | Tennessee | 0.304 | 0.869 | 26.91 | 0.972 | |
| Zinc | National Zinc Co. | Oklahoma | 0.572 | 0.979 | 23.7 | 0.97 | |
| Gold | Bernheim | S. Rhodesia | 0.87 | 0.38 | 42.7 | 1.77 | |
| Flint | Tri-State flint | Missouri | 0.930 | 0.279 | 29.4 | 1.54 | |
| Gold | Wright Hargreaves | Ontario | 1.24 | 0.556 | 44.0 | 1.70 | 2.68 |
| Gold | Kelowna Expl. Co. | B. Columbia | 1.37 | 0.640 | 47.5 | 2.09 | 3.217 |
| Gold | Noranda | Quebec | 1.468 | 0.65 | 44.9 | 1.85 | 2.85 |
| Gold | Portland | Colorado | 1.64 | 0.592 | 36.7 | 1.63 | 2.69 |
| Gold | Little Long Lac | Ontario | 1.826 | 0.704 | 41.4 | 1.69 | 2.64 |
| Gold | Round Mountain | Nevada | 1.96 | 0.553 | 34.9 | 1.61 | |
| Gold | East Rand | S. Africa | 1.985 | 0.654 | 36.0 | 1.78 | 2.71 |
| Copper | Phelps Dodge | Arizona | 2.10 | 0.767 | 40.0 | 1.63 | 2.68 |
| Gold | Benguet Cons. | Philippine Islands | 2.19 | 0.698 | 38.0 | 1.69 | 2.66 |
| Gold | San Fernando-B | Mexico | 2.28 | 0.766 | 34.6 | 1.56 | |
| Gold | San Fernando-A | Mexico | 2.31 | 0.812 | 35.8 | 1.56 | |
| Gold | Saramarca | Peru | 2.39 | 0.744 | 32.4 | 1.815 | |
| Garnet | Garnet | Georgia | 2.40 | 1.063 | 36.5 | 1.78 | |
| Phosphate | Al-Ke-Me | | 2.41 | 0.688 | 32.9 | 1.39 | |
| Copper | Miami Copper Co. | Arizona | 2.61 | 0.978 | 38.2 | 1.64 | 2.69 |
| Lead-zinc | Montecatini | Italy | 2.69 | 0.794 | 31.4 | 2.32 | |
| Quartz | Pure crystallized | California | 2.72 | 0.703 | 27.1 | 1.68 | 2.65 |
| Gold | Homestake | S. Dakota | 2.95 | 1.250 | 45.1 | 1.91 | 3.12 |
| Copper-zinc | Sherritt Gordon | Manitoba | 2.97 | 0.892 | 31.2 | 1.85 | |
| Copper-lead | Cons. Copper | Nevada | 3.00 | | 35.0 | 1.54 | |
| Shale | St. Lawrence brick | Quebec | 3.50 | 1.534 | 40.0 | 1.585 | |
| Copper | Tennessee Copper | Tennessee | 4.80 | 1.286 | 30.2 | 2.08 | |
| Copper-phosphorus | Cons. Copper | Nevada | 5.32 | | 38.2 | 1.64 | |
| Copper | Bingham Canyon | Utah | 5.90 | 1.73 | 30.7 | 2.68 | 4.65 |
| Zinc | Farrey Company | Illinois | 6.74 | | | 1.74 | |
| Graphite | Congdon | Alabama | 9.26 | 2.14 | 24.5 | 1.35 | |
| Galena | Eagle Picher | Missouri | 13.5 | 3.77 | 27.6 | 4.61 | |

TABLE 1.—(*Continued*)

| Ore | Description | Location | Net Grams per Revolution | | −200 Mesh in Product, Per Cent | Specific Gravity | |
|---|---|---|---|---|---|---|---|
| | | | | | | Apparent | True |
| TESTS AT MINUS 65 MESH | | | −65 Mesh | −200 Mesh | | | |
| C.I. | Miami Copper | Arizona | 0.061 | 0.017 | 29.3 | 3.51 | 7.07 |
| Emery | Amer. Emery Wheel | Rhode Island | 0.459 | 0.235 | 51.2 | 2.47 | 3.89 |
| Gold | Kelowna Expl. Co. | B. Columbia | 1.24 | 0.657 | 54.4 | 2.09 | 3.217 |
| Gold | Little Long Lac | Ontario | 1.490 | 0.720 | 50.85 | 1.69 | 2.64 |
| Copper | Britannia M. and S. | B. Columbia | 1.577 | 0.606 | 39.1 | 1.71 | |
| Gold | A. O. Smith | Colorado | 1.583 | 0.765 | 54.2 | 1.60 | |
| Coal | Illinois Zinc | Illinois | 1.61 | 0.775 | 47.8 | 1.70 | 2.80 |
| Gold | East Rand | S. Africa | 1.717 | 0.718 | 44.67 | 1.78 | 2.71 |
| Gold | Madsen Red Lake | Ontario (?) | 1.73 | 0.656 | 40.50 | 1.70 | 2.65 |
| Gold | Benguet Cons. | Philippine Islands | 1.75 | 0.718 | 46.49 | 1.69 | 2.66 |
| Gold | G. E. Smith—Portland | Oregon | 1.85 | 0.675 | 37.9 | 1.60 | |
| Granite | Picacho mine | Arizona | 1.877 | 0.693 | 39.32 | 1.53 | 2.64 |
| Gold | Spring Hill gold mines | California | 1.903 | 0.827 | 45.89 | 1.70 | |
| Iron | Bowering-Keradid | Morocco | 1.94 | 0.693 | 36.8 | 1.86 | |
| Copper | Phelps-Dodge | Arizona | 2.022 | 0.839 | 45.0 | 1.63 | 2.68 |
| Copper | Chelan Copper | Washington | 2.07 | 0.890 | 44.5 | 1.64 | |
| Copper-lead | Cons. Copper Co. | Nevada | 2.10 | 0.890 | 43.7 | | |
| Copper | Cyprus mines | Cyprus | 2.11 | 0.906 | 43.4 | 2.69 | |
| Gold | Stadacona | Quebec | 2.157 | 1.090 | 53.2 | 1.895 | |
| Apatite | Ipanema Phosphorus | Brazil | 2.255 | 0.85 | 42.8 | 2.36 | 3.99 |
| Gold | Santa Maria del Oro | Mexico | 2.31 | 1.072 | 49.47 | 2.08 | 3.097 |
| Lead | Montecatini | Italy | 2.39 | 1.00 | 42.6 | 2.32 | |
| Gold | Parcoy Gold | Peru | 2.393 | 0.683 | 31.30 | 2.26 | |
| Gold | Minn. mines | Colorado | 2.42 | 0.963 | 43.0 | 1.85 | 2.81 |
| Gold | Ipo gold | Philippine Islands | 2.61 | 0.878 | 37.2 | 1.68 | |
| Gold | A. O. Smith | Colorado | 2.675 | 1.428 | 55.0 | 1.48 | |
| Salt | Mines D.deP. | France | 2.685 | 0.627 | 22.9 | 1.321 | |
| Copper-phosphorus | Cons. Copper | Nevada | 3.63 | | 46.0 | 1.64 | |
| Ferromanganese | Champion Rivet Co. | Ohio | 4.523 | 1.545 | 35.0 | 4.64 | |
| Fluorspar | Alum. Ore Co. | Missouri | 5.700 | 1.982 | 35.0 | 1.88 | 2.98 |
| TESTS AT MINUS 100 MESH | | | −100 Mesh | −200 Mesh | | | |
| Coke | Aluminum Co. of America | Tennessee | 0.19 | 0.103 | 55.96 | 0.972 | |
| Gold | Charles Butters | Nicaragua | 0.393 | 0.221 | 56.7 | 1.52 | |
| Gold | Portland | Colorado | 0.513 | 0.295 | 56.6 | 1.63 | 2.69 |
| Flint | Tri-State flint | Missouri | 0.618 | 0.331 | 52.6 | 1.54 | |
| Gold | Bernheim | S. Rhodesia | 0.790 | 0.474 | 60.0 | 1.77 | |
| Gold | Veraguas | Panama | 0.832 | 0.593 | 71.8 | 1.75 | 2.78 |
| Abrasive | Monsanto Chem. | Alabama | 0.858 | 0.263 | 30.2 | 2.11 | 3.91 |
| Gold | Wright-Hargreaves | Ontario | 0.980 | 0.594 | 61.0 | 1.70 | 2.68 |
| Gold | Kelowna Expl. Co. | B. Columbia | 1.01 | 0.672 | 67.5 | 2.09 | 3.217 |
| Gold | Noranda | Quebec | 1.079 | 0.776 | 69.9 | 1.85 | 2.85 |
| Gold | Little Long Lac | Ontario | 1.150 | 0.772 | 67.8 | 1.69 | 2.64 |
| Quartz | Wheeler-Como mines | Nevada | 1.288 | 0.787 | 62.7 | 1.685 | 2.61 |
| Gold | East Rand | S. Africa | 1.323 | 0.806 | 62.3 | 1.78 | 2.71 |
| Tailings | W. A. Ledell Co. | Texas | 1.335 | 1.39 | 80.8 | 1.75 | 2.59 |
| Phosphate | Al-Ke-Me | | 1.36 | 0.809 | 61.8 | 1.39 | |
| Gold | Lucky Coon | Ontario | 1.46 | 0.811 | 55.8 | 1.635 | |
| Apatite | Ipanema phosphorus | Brazil | 1.470 | 0.818 | 59.6 | 2.36 | 3.99 |
| Gold | Mamre, East Rand | S. Africa | 1.483 | 0.714 | 49.1 | 1.90 | |
| Copper | A. E. Wheeler | Belgian Congo | 1.49 | 0.868 | 62.9 | 1.32 | |
| Silver | Cia. Min. Carlota | Chile | 1.51 | 1.091 | 72.0 | 1.878 | 3.00 |
| Gold | Madsen Red Lake | Ontario | 1.515 | 0.781 | 53.4 | 1.70 | 2.65 |
| Quartz | Pure crystallized | California | 1.523 | 0.793 | 53.0 | 1.68 | 2.65 |
| Gold | Getchell mine | Nevada | 1.535 | 0.910 | 59.3 | 1.428 | |
| Copper | Phelps Dodge | Arizona | 1.57 | 0.966 | 63.1 | 1.63 | 2.68 |
| Gold | Santa Maria del Oro | Mexico | 1.575 | 0.912 | 60.21 | 2.08 | 3.097 |
| Gold | Dahlonega gold | Georgia | 1.58 | 0.811 | 51.9 | 1.67 | |
| Copper | Sherritt Gordon | Manitoba | 1.64 | 0.935 | 57.0 | 1.85 | |
| Gold | Empire Star | California | 1.752 | 0.962 | 56.58 | 1.78 | |
| Copper | Cyprus mines | Cyprus | 1.786 | 1.07 | 60.3 | 2.69 | |
| Gold | Fred Viles | Montana | 1.81 | 1.172 | 63.92 | 1.72 | |
| Copper | Miami Copper Co. | Arizona | 1.816 | 0.92 | 52.2 | 1.64 | 2.69 |
| Gold | Rochester Plymouth | Nevada | 1.860 | 1.121 | 63.14 | 1.83 | 2.75 |
| Gold | Homestake | S. Dakota | 1.964 | 0.806 | 66.5 | 1.78 | 2.71 |

TABLE 1.—(*Continued*)

| Ore | Description | Location | Net Grams per Revolution | | −200 Mesh in Product, Per Cent | Specific Gravity | |
|---|---|---|---|---|---|---|---|
| | | | | | | Apparent | True |
| TESTS AT MINUS 100 MESH | | | −100 Mesh | −200 Mesh | | | |
| Gold | Ipo gold | Philippine Islands | 2.01 | 1.015 | 52.9 | 1.68 | |
| Fertilizer | Int. Agric. Corp. | Florida | 2.260 | 1.172 | 47.3 | 1.50 | |
| Nickel | Falconbridge nickel mine | Ontario | 2.405 | 1.38 | 59.3 | 2.29 | 3.65 |
| Carbonate | Carbonate iron ore | Michigan | 2.50 | 1.47 | 79.2 | 2.17 | |
| Copper-phosphorus | Cons. Copper | Nevada | 2.590 | | 60.2 | 1.69 | |
| Iron | Bowring-Keradid | Morocco | 2.66 | 1.327 | 49.4 | 1.80 | |
| Copper | Bingham Canyon | Utah | 2.99 | 1.355 | 42.6 | 2.68 | 4.65 |
| Ferrous slag | Victor Chem. Co. | Tennessee | 4.15 | 3.33 | 75.2 | 4.05 | |
| TESTS AT MINUS 150 MESH | | | −150 Mesh | −200 Mesh | | | |
| Gold | Kelowna Expl. Co. | B. Columbia | 0.865 | 0.666 | 77.90 | 2.09 | 3.217 |
| Gold | Little Long Lac | Ontario | 1.080 | 0.893 | 82.60 | 1.69 | 2.64 |
| Gold | East Rand | S. Africa | 1.117 | 1.270 | 76.65 | 1.78 | 2.71 |
| Gold | H. C. Winans | Brazil | 1.155 | 0.882 | 76.8 | 1.63 | |
| Gold | Bong Mieu | Indo-China | 1.31 | 0.978 | 75.7 | 2.00 | 3.07 |
| Gold | Minn. Mines Corp. | Colorado | 1.368 | 1.050 | 77.6 | 1.85 | 2.81 |
| Copper | Mines de Bor | Serbia | 1.41 | 1.190 | 84.5 | 1.91 | |
| Gold | Can. Malartic | Quebec | 1.445 | 1.134 | 78.5 | 1.84 | |
| Gold | Parcoy | Peru | 1.495 | 1.095 | 72.76 | 2.26 | |
| Nickel | B. C. Nickel Mines | B. Columbia | 1.607 | 1.142 | 71.40 | 2.47 | |
| Gold | Buffalo-Ankerite | Ontario | 1.705 | 1.400 | 82.90 | 1.935 | |
| Gold | M. A. Smith (Fla.) | Cuba | 1.725 | 1.300 | 78.24 | 1.855 | |
| Lead-zinc | Callahan Zinc Lead | Idaho | 1.81 | 1.075 | 60.42 | 2.23 | |
| Gold | Preston E. Dome | Ontario | 2.01 | 1.728 | 86.82 | 1.78 | |
| Gold | Atienda | Italy | 2.84 | 2.265 | 84.35 | 1.42 | 2.56 |
| TESTS AT MINUS 200 MESH | | | | −200 Mesh | | | |
| Flint | Tri-State flint | Missouri | | 0.491 | | 1.54 | |
| Gold | Bernheim | S. Rhodesia | | 0.560 | | 1.77 | |
| Shale | Korite Corp | Wisconsin | | 0.59 | | 1.588 | |
| Rutile | Titanium Corp. | Arkansas | | 0.620 | | 2.36 | |
| Min. wool | Mineralite Corp. | Pennsylvania | | 0.678 | | 0.20 | |
| Iron | East. Mabellite | | | 0.719 | | 1.74 | |
| Gold | Kelowna Expl. Co. | B. Columbia | | 0.758 | | 2.09 | 3.217 |
| Gold | Wright-Hargreaves | Ontario | | 0.771 | | 1.70 | 2.68 |
| Gold | Cia. Min. Ciclon | Chile | | 0.788 | | 1.772 | |
| Clay | Sun Oil Co. | Pennsylvania | | 0.790 | | 0.657 | 1.095 |
| Gold | Noranda | Quebec | | 0.830 | | 1.85 | 2.85 |
| Gold | Mamre | S. Africa | | 0.842 | | 1.90 | |
| Gold | East Rand | S. Africa | | 0.859 | | 1.78 | 2.71 |
| Quartz | Pure Crystallized | California | | 0.878 | | 1.68 | 2.65 |
| Magnetite | Du Pont | Pennsylvania | | 0.89 | | 2.73 | |
| Gold | Little Long Lac | Ontario | | 0.903 | | 1.69 | 2.64 |
| Ilmenite | Krebs Pigment | Maryland | | 0.920 | | 2.79 | |
| Copper | Phelps Dodge | Arizona | | 0.942 | | 1.63 | 2.68 |
| Gold | Santa Maria del Oro | Mexico | | 0.980 | | 2.08 | 3.10 |
| Gold | M. A. Smith (Fla.) | Cuba | | 1.025 | | 1.855 | |
| Gold | Portland | Colorado | | 1.035 | | 1.63 | 2.69 |
| Gold | Berens River Mine | Ontario | | 1.045 | | 1.950 | |
| Gold | Cia. Min. Carlota | Chile | | 1.048 | | 1.878 | 3.00 |
| Copper | Vanadium Corp. | Pennsylvania | | 1.08 | | 2.44 | |
| Ilmenite | Gen. Mang. Corp. | S. Dakota | | 1.136 | | 1.622 | |
| Manganese | Miami Copper Co. | Arizona | | 1.139 | | 1.64 | 2.69 |
| Copper | Rochester Plymouth | Nevada | | 1.141 | | 1.83 | 2.75 |
| Gold | Baguio Gold Min. Co. | Philippine Islands | | 1.160 | | 1.62 | 2.63 |
| Gold | Ham. B. & W. | California | | 1.20 | | 1.70 | |
| Gold | Homestake | S. Dakota | | 1.26 | | 1.91 | 3.12 |
| Copper | Cyprus mine | Cyprus | | 1.284 | | 2.69 | |
| Lead | Monteponi | Italy | | 1.396 | | 2.88 | 4.43 |
| Zinc | N. Jersey Zinc Co. | Pennsylvania | | 1.482 | | 2.55 | |
| Gold | Preston East Dome | Ontario | | 1.69 | | 1.78 | |
| Copper | Bingham Canyon | Utah | | 1.854 | | 2.68 | 4.65 |
| Copper | Mines de Bor | Serbia | | 1.94 | | 2.10 | |
| Slag | Arcade Smelt. and Ref. | Massachusetts | | 5.16 | | 4.53 | |

grindability of the ore at the particular mesh size tested, and is proportional to the relative ease of grinding in commercial installations.

Table 1 gives the condensed results of a large number of grindability tests. Those for each mesh are arranged in the order of increasing ease of grinding. In addition to the grindability at the specified mesh, the net production of minus 200-mesh material in grams per revolution, the percentage of minus 200-mesh material in the mill product, and the apparent and true specific gravities, are included. The production of minus 200-mesh material is useful in making approximate comparisons between ores tested at different meshes. The apparent specific gravity is the specific gravity of the sample crushed to minus 6 mesh and packed by shaking. It is ordinarily about 60 per cent of the true specific gravity.

## 2. Screen Analyses and Surface Calculations

Any correct determination of the total work done in crushing or grinding that is to have more than a relative value should be based upon the amount of new surface produced, and the calculation of surface area can be no more accurate than the screen analysis from which it is derived. It was early determined that an ordinary screen analysis is not sufficiently exact for this purpose, and that refinements in the method are necessary if dependable data are to be obtained.

These refinements fall into two categories, which are: (1) an improved technique in manipulation to obtain the greatest possible accuracy from the screens used, and (2) a method of correcting the results for errors in the screens, so that a reported screen analysis shall give the size distribution according to the exact mesh size specified rather than according to the individual screens used.

The manipulation technique adopted is described in paper No. 2 as the wet-dry method. A split sample of about 100 grams of the material to be analyzed is washed on a special 200-mesh sieve with a stream of water from a rubber tube for several minutes, or until nearly all of the slimes have been removed. The sample is then dried and the loss of weight recorded, after which it is placed in a nest of Tyler standard screen scale sieves extending to 200 mesh, and agitated in a shaking device for 30 min. Each screen fraction is then weighed to the nearest tenth of a gram, and the per cent and per cent cumulative weights retained on each mesh size are calculated.

Some material is always retained on the 200-mesh sieve during washing, which passes it later during dry screening, since irregularly shaped particles near the limiting size can pass through more readily dry than wet. This material is included in the final minus 200-mesh fraction.

The method of correcting, or standardizing, the screens used is based upon the size-distribution law given in paper No. 2. This law states that when a homogeneous material is crushed or ground, and the logarithm of the per cent weight of the product retained upon each screen in the Tyler standard screen scale is plotted against the ordinal number of the screen, the lower part of the resulting curve is a straight line extending from the point of its inception to the finest screen used. The point of inception is usually only three or four ordinal numbers below the size of the largest particle present. The straight line, called the distribution line, can be extended beyond the finest screen to the grind limit, or colloidal size range.

A search was conducted for a suitable homogeneous material, and petroleum coke was found to be satisfactory. Samples were crushed to minus 6 mesh and screen-analyzed. The correct per cent weight retained on 200 mesh was determined with a special standardized screen from the U. S. Bureau of Standards. This fixed the 200-mesh point on the distribution line. The screen analyses showed that the line was straight near its inception, and this portion was considered to be correct, since it is known that the coarse screens vary little if any from their designated sizes. This established the correct distribution line, and the variation of the plotted results of the screen analyses from it showed the error at each screen size. A correction factor was applied to each screen to make the resulting log per cent weight retained fall directly upon the distribution line, and this correction factor is applied to all screen analyses.

One corrected set of sieves is used in making all screen analyses, and the correction factors are redetermined periodically. When the plotted distribution line shows a marked variation from a straight line at any size, and this variation continues for analyses of different classes of materials, it is usually an indication of a change in the screen, caused either by wear or by blinding.

The use of the wet-dry method and correction factors, as described above, have greatly improved the accuracy of our screen analyses and of the surface areas computed from them.

The principal factors that make possible the evaluation of a screen analysis and the computation of surface area from it are the slope $m$ of the distribution line, and the existence of a grind limit.

Ordinal numbers $n$ are assigned to the various screen sizes in such a manner that if $d$ is the average grain diameter in microns (or thousandths of a millimeter) of particles retained on any screen $n$, and passing the next larger screen $n + 1$,

$$d = a\sqrt{2^{n-1}} \qquad [1]$$

where $a$ is a constant such that

$$\log a = \bar{5}.9285948 \qquad [2]$$

For screens in the Tyler standard screen scale $n$ is always a whole number; $n$ is 41 for 200 mesh, 42 for 150 mesh, and so on up the screen scale.

The grind limit is the inception of the colloidal size range. It is assumed that in an ordinary ore grind the production of colloidal material does not represent the direct expenditure of work, but rather the exposure and release of particles that existed in the colloidal state in the interstices of the ore prior to grinding. Determinations show that most of the clayey material in an ore is released by crushing to about minus 10 mesh, and further grinding, even to all through 200 mesh, results in the production of little or no additional colloidal material.

Ordinal number 28 is considered as the lower limit of an ore grind under usual conditions. This is equivalent to a limiting diameter of 0.818 microns, which for our purpose is defined as the inception of the colloidal size range. All material above this size is delineated by the distribution line; it is assumed to have been produced directly by comminution, and its surface area is used to calculate the work done in crushing and grinding.

The slope $m$ of the distribution line is ordinarily computed as the average slope between 65 and 200 mesh, or ordinals 44 and 41, where the line is approximately straight. Of course, if the point of inception of the line is below 65 mesh, only the average of the slopes below this point can be used. Taking the average slope in this manner tends to equalize the mechanical errors retained in the corrected screen analysis, and gives more accurate results.

$P$ represents the corrected per cent weight passing 150 mesh and retained on 200 mesh. It has been found preferable to compute the average value of $P$ from the slope $m$ rather than to take it directly from the screen analysis; $0.3m$ is subtracted from the sum of the log per cent weights retained on 100, 150 and 200 mesh, and one-third of the difference is the logarithm of the corrected value of $P$.

If we let $U$ represent the percentage of colloidal material, or unground fines, in the ore, $F$ the per cent weight of the total minus 200-mesh material, as determined by the corrected screen analysis, and $G$ the percentage of noncolloidal minus 200-mesh material,

$$U = F - G \qquad [3]$$

It can be shown that $G$ can be computed from $m$ and $P$ by the following formula:

$$G = \frac{4.343P}{m}\left[1 - \frac{1}{\text{antilog }(1.3m)}\right] \qquad [4]$$

The total surface area $S_n$ of 1 c.c. of solid material which all passes screen $n + 1$ and is retained on screen $n$ is

$$S_n = \frac{6}{a\sqrt{2^{n-1}}} \text{ sq. meters} \qquad [5]$$

The total surface area $S_{41}$ of the noncolloidal minus 200-mesh portion of a sample of 100 c.c. of solid material is

$$S_{41} = \frac{0.2929P}{1.505 - m}\{\text{antilog}\,[1.3(1.505 - m)] - 1\} \qquad [6]$$

To compute the total noncolloidal surface area of 100 c.c. of solid from a corrected screen analysis several steps are necessary. The average values of $m$ and $P$ and $F$ must be found from the screen analysis: then $G$ is computed from eq. 4, $U$ from eq. 3, and $S_{41}$ from eq. 6.

13

TABLE 2.—*For Calculation of Surface Areas of Screen Fractions*

| Mesh | $n$ (Screen number) | $d$ (microns) | Surface per Cubic Centimeter, Sq. M. |
|---|---|---|---|
| Inch | | | |
| 2 | 60 | 64,360 | 0.0000931 |
| 1½ | 59 | 45,520 | 0.0001317 |
| 1 | 58 | 32,180 | 0.0001863 |
| ¾ | 57 | 22,760 | 0.0002635 |
| ½ | 56 | 16,090 | 0.000373 |
| ⅜ | 55 | 11,376 | 0.000527 |
| Mesh | | | |
| 3 | 54 | 8,052 | 0.000745 |
| 4 | 53 | 5,694 | 0.001054 |
| 6 | 52 | 4,026 | 0.001490 |
| 8 | 51 | 2,847 | 0.002108 |
| 10 | 50 | 2,013 | 0.002980 |
| 14 | 49 | 1,423 | 0.00422 |
| 20 | 48 | 1,006.5 | 0.00596 |
| 28 | 47 | 711.7 | 0.00843 |
| 35 | 46 | 503.2 | 0.01192 |
| 48 | 45 | 355.8 | 0.01686 |
| 65 | 44 | 251.6 | 0.02385 |
| 100 | 43 | 177.9200 | 0.0337 |
| 150 | 42 | 125.8112 | 0.0477 |
| 200 | 41 | 88.9600 | 0.0675 |
| 270 | 40 | 62.9056 | 0.0954 |
| 400 | 39 | 44.4800 | 0.1349 |
| | 38 | 31.4528 | 0.1908 |
| | 37 | 22.2400 | 0.2698 |
| | 36 | 15.7264 | 0.3815 |
| | 35 | 11.1200 | 0.5396 |
| | 34 | 7.8632 | 0.7630 |
| | 33 | 5.5600 | 1.079 |
| | 32 | 3.9316 | 1.526 |
| | 31 | 2.7800 | 2.158 |
| | 30 | 1.9658 | 3.052 |
| | 29 | 1.3900 | 4.316 |
| | 28 | 0.9829 | 6.104 |

The surface area of the plus 200-mesh portion is computed from Table 2. This table is constructed from eq. 5, so that the surface area of each screen fraction is found by multiplying $S_n$ for that fraction by the per cent weight retained.

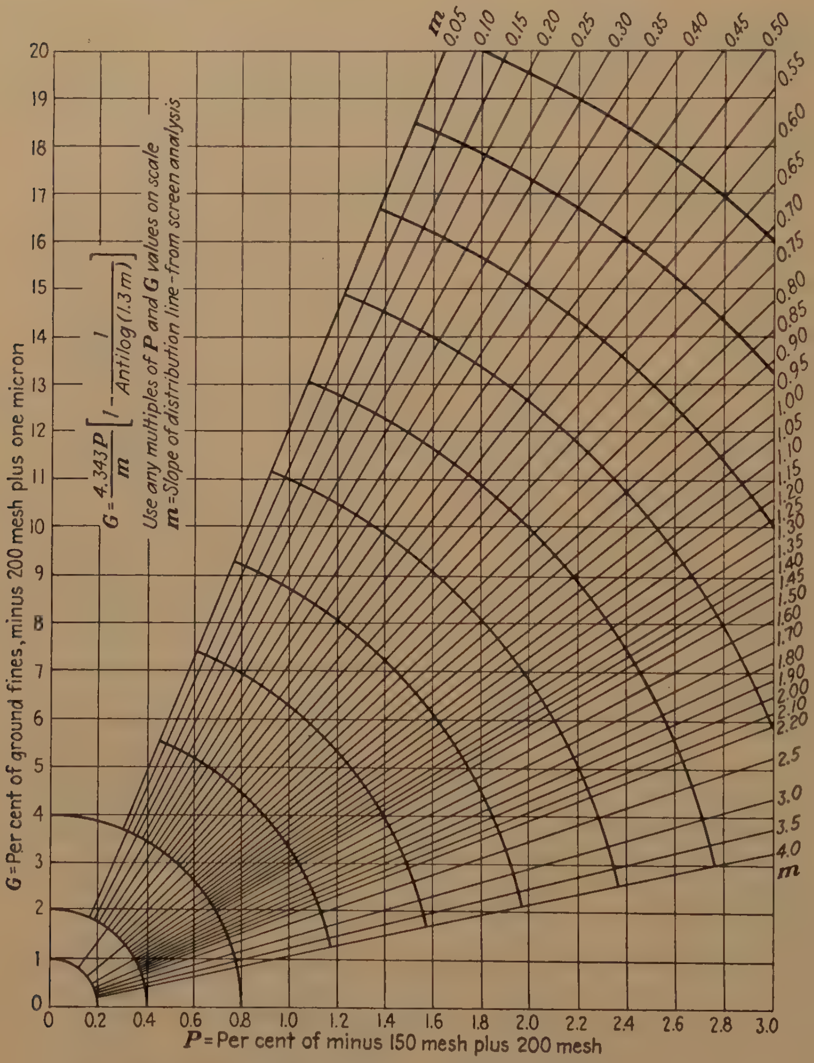


FIG. 1.—CHART NO. 1, FOR SOLVING EQUATION 4.

The total surface area is the sum of $S_{41}$ and the surface areas of the plus 200-mesh screen fractions. It is expressed as square meters per 100 c.c. of solid sample, excluding void space.

In order to facilitate the computations, charts (Figs. 1 and 2) have been prepared by means of which equations 4 and 6 can be solved graphically by merely locating the given values of $P$ and $m$. The charts include values of $P$ up to 3.00 per cent, but can be used for any value of $P$ merely by dividing by such a number that the quotient is less than 3 per cent, and multiplying the corresponding value of $G$ or $S_{41}$ by the same number. When the values of $U$ and $G$ are known or assumed, chart No. 1 can also be used to find the value of $m$ corresponding to the given value of $P$.

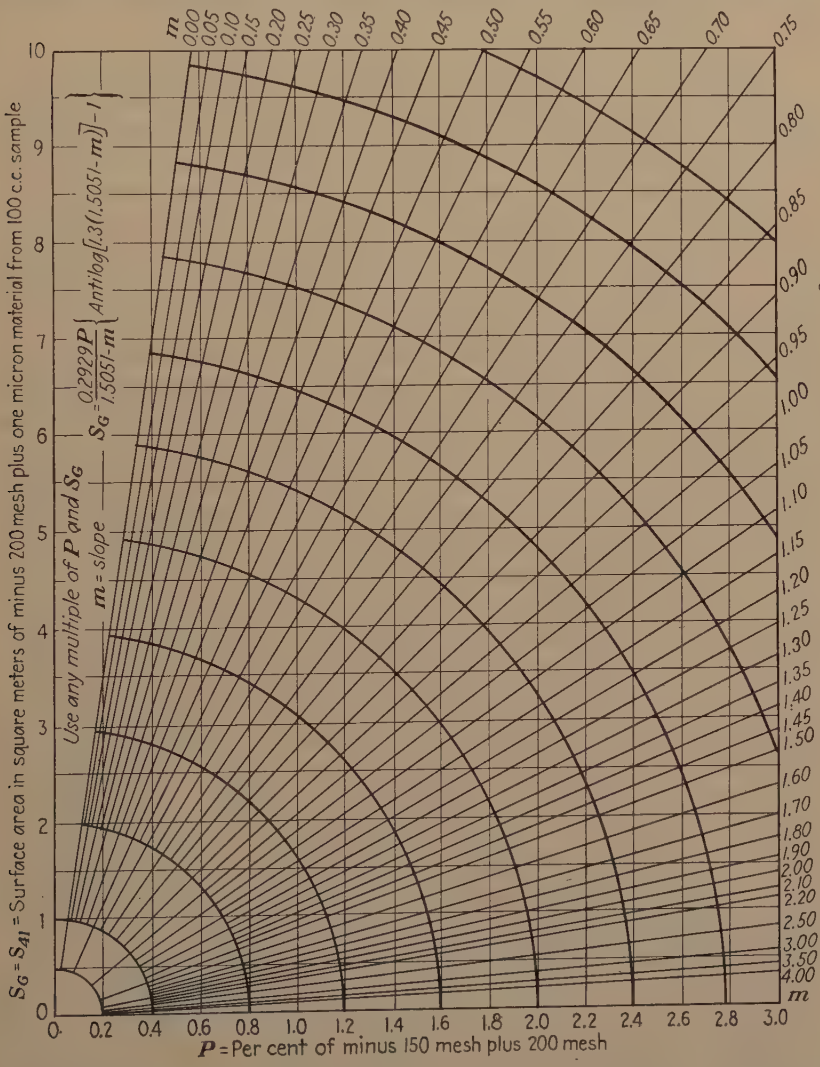


FIG. 2.—CHART No. 2, FOR SOLVING EQUATION 6.

A calculation made with the aid of the charts is not particularly laborious, since slide-rule accuracy is sufficient. However, judgment must be exercised when occasional erratic values of $U$ or $m$ are encountered, due to faulty screen analyses. $U$, or the percentage of colloidal material, is usually between 0.5 and 3.0 per cent. If a large amount of clay is present it may be more; if clayey material is completely absent it may be slightly less, but most ores will fall within these limits, with an average value of 1.5 to 2.0 per cent. It has been found preferable to determine the percentage of colloidal material from the screen analysis of the ore crushed to about minus 6 mesh, and to assign that value of $U$ to all more finely ground products, computing $G$ and $m$ from $U$ with the aid of the charts.

The method of calculation is essentially a wide extrapolation below 200 mesh, and unless the value of $U$ is controlled slight errors in the screen analysis give greatly magnified errors in the computed surface.

If the value of $U$, found from the screen analysis of a crushed sample, is used throughout for all finely ground samples, screen-analysis errors are minimized and consistent results on samples crushed as fine as all minus 200 mesh are probable. This is shown by data in part 4 of this paper. In special cases, where the slimes have been removed by washing or screening, $U$ is always assumed to be zero.

The slope $m$ of the distribution line is a significant quantity, which varies considerably with different materials and different conditions of comminution. It tends to increase slightly with finer grinding under similar conditions, and this fact can serve as a check upon the accuracy of the value of $U$ used. If $m$ decreases or increases rapidly with finer grinding, $U$ is evidently incorrect. In nearly all cases it is best to consider that the grind limit extends to ordinal 28, and to adjust $m$ accordingly.

TABLE 3.—*Specimen Calculation*

| Mesh | Per Cent Wt. | Cumulative Per Cent | Log Per Cent Wt. | Surface |
|---|---|---|---|---|
| On 65 | 0 | 0 | | 0 |
| 100 | 31.74 | 31.74 | 1.501 | 1.069 |
| 150 | 13.00 | 44.74 | 1.114 | 0.620 |
| 200 | 10.26 | 55.00 | 1.011 | 0.693 |
| −200 | 45.00 | 100.00 | | |
| | 100.00 | | | 2.382 |

$U$ = 2.11 per cent colloidal material
$P$ = 10.26 per cent from screen analysis, direct
$F$ = 45.00 per cent from screen analysis, direct
$G$ = 42.89 per cent $G = F - U$
$m$ = 0.98 from chart No. 1, by dividing $P$ and $G$ each by 4.
$S_{41}$ = 21.60 sq. m. from chart No. 2, using $m$ and $P/4$, and multiplying the surface by 4.

A specimen calculation is given in Table 3. The sample is the ball-mill product from standard grindability tests at 65 mesh on New Cornelia copper ore. The amount of colloidal material present has been determined from the screen analysis of the minus 6-mesh ball-mill feed to be 2.11 per cent.

The total surface area $S_T$ is 21.60 plus 2.38, or 23.98 sq. m. per 100 c.c. of solid sample. The surface of the ball-mill feed was 6.07 sq. m. per 100 c.c., so the new surface made is 17.91 sq. m. The mill production was 2.461 gross grams, or 0.919 c.c. per revolution, and 0.919 multiplied by 0.1791 sq. m. per cubic centimeter gives 0.1645 sq. m. of new surface produced per revolution of the mill.

The surface energy of this ore has been measured by the method described in part 3 as 295.7 joules per square meter, and this multiplied by the new surface produced gives 48.65 joules of useful work done per revolution of the mill.

## 3. Measurement of Surface Energy by Pendulum Impact Tests

If the absolute power efficiency of a crushing or grinding operation is to be measured, the amount of work necessary to produce a unit area of new surface of the material must be known. For our purposes we define this quantity as the surface energy, or the work in joules necessary to produce one square meter of new surface. Any discussion as to whether this is the actual surface energy of the solid will be deferred to part 4.

Any device that will measure this surface energy must be so constructed that a known amount of work is done on the sample to be tested —in other words, so that the net work input to the sample can be measured. The usual arrangement[3] is a block of hardened steel placed on an anvil and containing a cylindrical well, in which the sample to be crushed is placed under a closely fitting steel piston. A known mass is dropped a measured distance onto the piston, so that the force of the blow striking the piston is known. A part of the force of the blow is probably transmitted through the sample and absorbed by the anvil, and measurements of the magnitude of this part are somewhat uncertain.

These measurements are made by placing several soft wires between the block and the anvil before crushing, and applying a correction according to the amount that the wires are flattened to obtain the net work input. Blank tests, in which no sample is crushed, are made in order to obtain the correction factor.

The pendulum impact crushing device described here was designed in the mining division of the Allis-Chalmers Mfg. Co. expressly to avoid the absorption of energy by the supports. It is constructed to fit into the pendulum of an Amsler pendulum impact testing machine, in such a way that the energy of the falling pendulum is transmitted through a standard test bar, which is broken in tension in each test, to the rock to be crushed, and the excess energy not used in crushing the rock or in breaking the test bar is measured by a cursor marking the rise of the pendulum after the rock has been crushed.

The apparatus consists of a hardened steel block containing a cylindrical cavity, or well, and a closely fitting steel piston, which is connected by tension rods and crosshead to the standard test bar, ¼ in. in diameter and 1¼ in. long, which is to be broken in the test. The test bar is threaded into a cross member which engages stationary stops as the pendulum falls, and breaks the bar. (Figs. 3 and 4.)

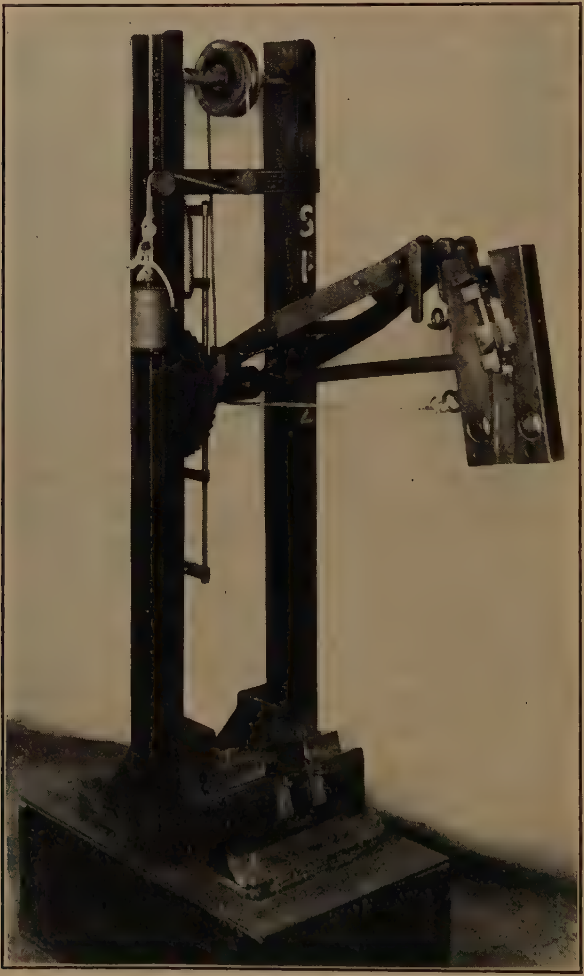


FIG. 3.—IMPACT CRUSHING DEVICE MOUNTED IN PENDULUM OF AMSLER PENDULUM IMPACT TESTING MACHINE.

In operation a 10-gram sample of the material to be tested is placed in the well, and the piston adjusted to rest lightly upon the sample. The device is inserted into the pendulum of the Amsler machine, which is dropped from a known position, breaking the test bar and crushing the sample. The rise of the cursor on the Amsler machine measures the excess kinetic energy remaining in the pendulum after the rock has been crushed and the bar broken, so that the work done on both is known. Blank determinations are made, in which the test bars are broken without crushing any rock, and the breaking strength of the bars determined. The excess energy consumed represents the work done in crushing the sample.

The test bars are machined automatically to the same size from the same stock, and the blank determinations made on them check closely.

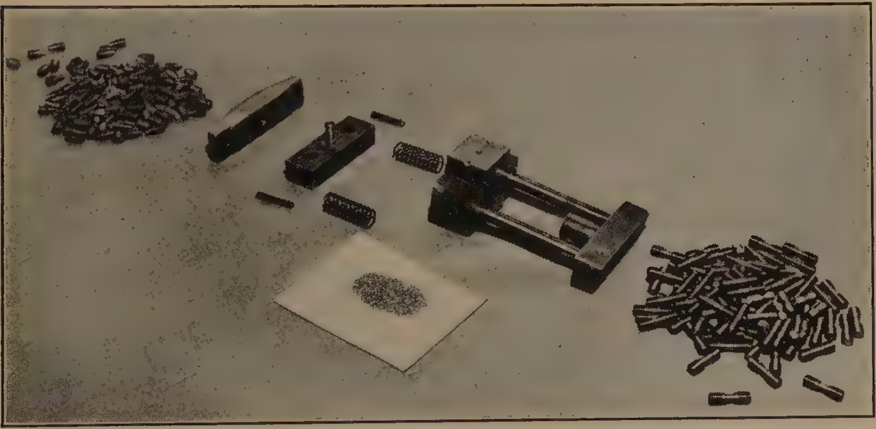


FIG. 4.—IMPACT CRUSHING DEVICE DISASSEMBLED, SHOWING ORE SAMPLE AND NEW AND BROKEN TEST BARS.

The sample used may be of any screen size, but for uniformity of procedure it is usually prepared by crushing the material to minus 6 mesh in closed circuit in rolls, and using the minus 14 plus 20-mesh fraction. Several 10-gram samples are crushed by impact, and the total work input in joules is recorded. Then a complete screen analysis is made on the combined samples of crushed material, and the total amount of surface is calculated according to the method described in part 2.

The new surface produced in crushing is computed by subtracting the total surface before crushing from that after crushing, and the remainder is divided into the net work done in joules. The result is the surface energy of the material in joules per square meter.

## 4. TEST RESULTS AND DISCUSSION

When the surface energy of an ore has been determined, and the amount of work necessary to produce a unit of new surface in a crusher or grinding mill has been calculated, the absolute power efficiency of the crusher or grinding mill is merely the ratio between these two quantities.

Until recently no acceptable calculations as to the absolute efficiency of grinding, as contrasted to relative efficiency, have been made, and common conceptions on this important subject have been quite vague. In years past the prevailing idea has been that the power efficiency was extremely low, perhaps of the order of from 1 to 4 per cent, making a ball mill one of the most inefficient of the known devices in common use.

More recent figures have modified these ideas considerably, and ball milling is now on at least a pseudorespectable basis. Grinding efficiencies of the order of from 25 to 45 per cent have been reported[3] in the dry grinding of cement clinker, and the wet grinding of ores to a relatively coarse mesh size should show a still higher efficiency. It is now to be hoped that this trend does not continue to the point where attempts to improve the efficiency are abandoned as futile.

The methods of measuring surface area and energy previously described were developed in an attempt to determine power efficiencies. Several determinations have been made, and while they are not sufficiently numerous as yet to be conclusive they are important and interesting in several respects.

Series of grindability tests have been made at the various meshes from 28 to 200, and the amount of new surface produced per revolution of the mill computed for each test. About ten different ores and other materials have been so treated, and they all show, *without exception*, that the new surface area produced per revolution of the mill is the same for all of the various meshes. In other words, one revolution of the mill will produce the same amount of new surface for the particular material being tested, independent of whether it is being ground to minus 28 mesh, to minus 200 mesh, or to any size between. Several computations have also been made at varying circulating loads, and these all show the same surface production per revolution, independent of the amount of the circulating load. These data are so uniform and consistent that we believe they conclusively establish the following two points:

1. The useful work done in grinding is proportional to the new surface area produced; in other words, Rittinger's law is the correct expression of the work done.

2. The grind limit of 0.818 microns and the method of computing surface areas from screen analysis outlined in part 2 are substantially correct, since they introduce no systematic variations from Rittinger's law in determinations covering a wide range of conditions.

These results show that an equal amount of useful work is done per revolution of the mill, when the same ore is ground to various mesh sizes and under varying conditions, and they suggest that the amount of work done per revolution may be constant when different materials are ground. Surface-energy determinations were made on several of the ores tested according to the method described in part 3, and this possibility was explored.

The results are tabulated below:

### *New Cornelia Ore*

These tests were made on a sample of mill feed of New Cornelia copper ore from Ajo, Ariz. The average of several pendulum impact tests showed that the ore has a surface energy of 295.7 joules per square meter. It contains 2.11 per cent colloidal material.

TABLE 4.—*Tests on New Cornelia Ore*

| Mesh Tested | Circulating Load | Net Grams per Revolution | $m$ | Per Revolution | |
|---|---|---|---|---|---|
| | | | | Sq. Meters | Joules |
| 28 | 250 | 2.50 | 0.77 | 0.1821 | 53.85 |
| 35 | 250 | 2.31 | 0.82 | 0.1778 | 52.60 |
| 48 | 250 | 2.10 | 0.925 | 0.1575 | 46.58 |
| 65 | 250 | 2.02 | 0.98 | 0.1645 | 48.60 |
| 100 | 250 | 1.57 | 1.025 | 0.1764 | 52.12 |
| 200 | 250 | 0.942 | 1.05 | 0.1614 | 47.70 |
| 65 | 150 | 1.83 | 0.95 | 0.1813 | 53.61 |
| 65 | 250 | 2.02 | 0.98 | 0.1645 | 48.60 |
| 65 | 400 | 2.33 | 0.96 | 0.1876 | 55.50 |
| 65 | 800 | 2.39 | 1.02 | 0.1696 | 50.18 |
| Averages.... | | | 0.945 | 0.1731 | 51.19 |

The laboratory ball mill uses approximately 100 watts, or 85.7 joules per revolution, so that the grinding efficiency was approximately 59.7 per cent in the tests.

The power consumption in kilowatt-hours per ton ground and screen analyses of the mill feed and product were obtained from the plant at Ajo when grinding to 51.9 per cent through 200 mesh, and it was calculated from these data that 496.9 joules per square meter of new surface were required. The computed power efficiency is 295.7 ÷ 496.9, or 59.5 per cent.

### *Little Long Lac Ore*

These tests were made on a sample of mill feed from Little Long Lac gold mine, Ontario. The average of three pendulum impact tests showed that the ore has a surface energy 306.8 joules per square meter. It contains 2.00 per cent of colloidal material. All of the standard grindability tests were made at 250 per cent circulating load.

TABLE 5.—*Tests on Little Long Lac Ore*

| Mesh Tested | Net Grams per Revolution | *m* | Per Revolution | |
|---|---|---|---|---|
| | | | Sq. Meters | Joules |
| 35 | 2.350 | 0.80 | 0.1793 | 54.95 |
| 48 | 1.825 | 0.825 | 0.1741 | 53.41 |
| 65 | 1.490 | 0.85 | 0.1726 | 52.95 |
| 100 | 1.150 | 0.89 | 0.1731 | 53.09 |
| 150 | 1.080 | 0.93 | 0.1759 | 53.93 |
| 200 | 0.903 | 0.96 | 0.1734 | 53.10 |
| Average...... | | 0.876 | 0.1747 | 53.57 |

The average grinding efficiency in the laboratory ball mill was approximately 62.5 per cent.

The ore is ground to 89 per cent through 200 mesh in practice. It was calculated from the power consumption and screen analyses of feed and product that 455.0 joules per sq. m. are required in commercial grinding. The computed power efficiency is 67.4 per cent.

### *Springs Mines Ore*

These tests were made on a sample of gold ore from Springs Mines, East Rand, South Africa. The surface energy of the ore was 462 joules per sq. m. as measured by pendulum impact tests. It contained 2.92 per cent colloidal material. All of the standard grindability tests were made at 250 per cent circulating load.

TABLE 6.—*Tests on Springs Mines Ore*

| Mesh Tested | Net Grams per Revolution | *m* | Per Revolution | |
|---|---|---|---|---|
| | | | Sq. Meters | Joules |
| 28 | 3.22 | 1.140 | 0.1103 | 50.95 |
| 35 | 2.404 | 1.070 | 0.1155 | 53.30 |
| 48 | 1.985 | 1.180 | 0.1132 | 52.25 |
| 65 | 1.717 | 1.272 | 0.1102 | 50.85 |
| 100 | 1.323 | 1.320 | 0.1127 | 52.05 |
| 150 | 1.117 | 1.300 | 0.1160 | 53.55 |
| 200 | 0.859 | 1.310 | 0.1122 | 51.80 |
| Averages..... | | 1.227 | 0.1129 | 52.11 |

The average grinding efficiency in the laboratory ball mill was 60.8 per cent. No commercial grinding data were available.

### *Petroleum Coke*

A sample of petroleum coke from Alcoa, Tenn., was tested. Impact tests showed it to have a surface energy of 760 joules per sq. m. It contained no colloidal material.

After grinding the coke, the balls were smooth and shiny, whereas they are rough after grinding rock.

TABLE 7.—*Tests on Petroleum Coke*

| Mesh | Net Grams per Revolution | $m$ | Per Revolution | |
|---|---|---|---|---|
| | | | Sq. Meters | Joules |
| 48 | 0.304 | 1.61 | 0.01826 | 13.88 |
| 100 | 0.190 | 1.76 | 0.01740 | 13.23 |
| Averages..... | | 1.685 | 0.01783 | 13.55 |

The average grinding efficiency in the laboratory ball mill was 15.8 per cent. This low efficiency shows the polishing and lubricating effect of the coke upon the grinding balls. No commercial grinding data were available.

### *Cement Clinker*

Two samples of cement clinker submitted by the Portland Cement Association were tested in the pendulum impact device. The minus 20 plus 28-mesh screened samples used contained no colloidal material. Sample $N$ had a surface energy of 244.5 joules per sq. m. at 864 surface barrels per kw-hr; sample $Q$ had a surface energy of 300 joules per sq. m. at 705 surface barrels per kw-hr. Surface barrels per kilowatt-hour, the unit published by Wilson,[3] is obtained by dividing 211,100 by the surface energy in joules per square meter.

No standard ball-mill grindability tests were made.

Impact tests were made on the same material by the Portland Cement Association and the surface produced was measured with a turbidimeter. The results in surface barrels per kw-hr. averaged 9.6 per cent higher than ours.

In general, surface determinations of cement clinker tend to give a slightly lower result when measured by a turbidimeter than when calculated from screen analyses, and the drop-weight impact device tends to give a higher surface-area production per unit of work input than the pendulum impact device.

## 5. DISCUSSION

The results confirm Rittinger's law and tend to show that a constant amount of useful work is done per revolution of the mill when grinding different ores to different sizes. However, this is not true when materials that tend to lubricate or polish the grinding media are tested.

The calculated power efficiencies on the basis of surface areas are higher than had been expected. The laboratory ball mill under the conditions of standard grindability tests on ores does about 52.3 joules of useful work per revolution, with an average calculated power efficiency of approximately 61 per cent. The average computed efficiency in commercial wet, closed-circuit, grinding was 63.5 per cent.

The method of computing surface areas from screen analyses has been found to yield reasonable and consistent results, so that if a considerable error exists in these calculated power efficiencies it probably lies in the determination of surface energies. The computation is essentially a comparison between the work done in a ball mill and the work done in a special device where supposedly all of the net work input is transmitted to the sample. It has been learned that the use of different varieties of steel with different hardnesses in the impact crushing device causes considerable differences in the measured surface energy; the use of a harder steel reduces the measured surface energy, so it may well be that all of the recorded surface energies are too high. In this case the grinding efficiencies given above are too high.

This implies that an unmeasured portion of the work input is absorbed by the deformation within the elastic limit of the steel parts used in the device, and an unknown correction factor should be applied to each device to find the net work input to the sample.

Thus, the measured surface energies and calculated grinding efficiencies can be considered only as maximum values, or upper limits. Probably some correction factor that will lower these values is needed, but the amount of this factor is unknown.

In the grinding of cement clinker, control was formerly based upon screen analyses, and the operating conditions, such as size of grinding media, mill speed, etc., were adjusted to make a product of the desired fineness (or percentage passing a 200-mesh screen) most efficiently.

At the present time the method of control is changing from screen analyses to a measurement of the specific surface area of the product by the turbidimeter method. It is apparent that grinding to produce a certain percentage through 200 mesh, and grinding to produce a certain surface area per gram of product, are distinctly different objectives, and that the most efficient grinding conditions from the standpoint of screen analyses may not be the most efficient from the standpoint of new surface produced.

The situation in respect to ore grinding is somewhat analogous to this, although as yet there is no standard method of control other than screen analyses. The object in grinding an ore is to unlock or expose the valuable minerals that are to be concentrated or dissolved. The usual method is to determine by tests the suitable mesh size that will yield the desired results, and to make this mesh size the sole criterion of the grinding operation.

We will assume that it has been decided to grind to 90 per cent through 200 mesh, and all of the grinding conditions, including the amount of the circulating load, are adjusted to make this product most efficiently. It has been found in our laboratory[4] that as the circulating load is increased a product of the desired mesh size is produced more efficiently up to a certain critical circulating load, and any further increase results in little or no gain in the net tonnage of a given mesh size. This critical circulating load varies rather widely for different ores, and for different mesh products from the same ore.

It has been shown in this paper, and confirmed by considerable unpublished data, that the amount of new surface produced per revolution of a mill remains essentially constant for wide variations in the amount of the circulating load, as it does for wide variations in the fineness of grinding.

This may appear inconsistent with the larger tonnage produced by an increased circulating load. It actually is not, because when the circulating load is augmented the slope of the distribution line becomes steeper, with less material in the finer grain sizes. In other words, a rigid distinction should be made between evaluation of results by measuring surface as compared with measurement by screen sizing.

However, a little thought will convince one that neither screen analyses nor surface measurements are the true criterion of efficiency in ore grinding. The most efficient ore grind is the one that produces the greatest amount of economic *unlocking*—or, in a dissolution process the greatest amount of exposure—of the valuable minerals with the least power consumption or lowest cost per ton. The gangue minerals should be removed from the grinding circuit as soon as they are ground fine enough to be separated from the ore minerals, and the middling particles should be reground only to the point of separation. Because the ore minerals have a higher specific gravity than the gangue minerals, the action of a classifier in effecting this separation and removal of the gangue is probably much more efficient than is indicated by screen analyses of the products.

It follows that the unlocking efficiency, or true efficiency in ore grinding, increases more rapidly with increasing circulating loads, and has a higher critical circulating load, than the efficiency as measured on a mesh-size basis. Screen analyses alone in a wet closed-circuit grinding system do not measure directly the unlocking efficiency, except in the almost nonexistent case where the ore and gangue minerals have the same specific gravity. It would appear that the correct determination of unlocking efficiency might involve the determination of the percentage of the ore minerals in the various parts of the grinding circuit.

The term *grinding efficiency* has several different meanings, with correspondingly different numerical values. They include *unlocking* efficiency, which is the correct measure of efficiency in ore grinding, but which is an indeterminate quantity at present; *new surface* efficiency, which might also be termed Rittinger efficiency; and *mesh size* efficiency, which is the one in common use. Each of these efficiencies can be expressed in terms of power consumption, mill size, operating cost, etc., so that many different opinions as to what constitutes efficient grinding are possible.

The most inclusive term is *economic* efficiency, or the unlocking efficiency on the basis of the total cost per ton; however, it includes so many factors that comparisons made on this basis are difficult and ineffectual. Grinding efficiency is a very general term; it is desirable that all of the limitations be fully understood and expressed if valid comparisons are to be made.

## SUMMARY

The results of a large number of standard closed-circuit grindability tests on different ores at different mesh sizes are tabulated in the order of increasing ease of grinding for each mesh.

A method of standardization of testing sieves and the correction of screen analyses is described, together with the technique of making a wet-dry analysis.

The calculation of the surface area from screen-analysis results by means of the distribution line is described and discussed. Two charts, which simplify the calculations, are included.

The pendulum impact device for measuring the surface energy of ores is described, and some of the results obtained with it are given. The surface energy as measured by this device may be too high.

A number of tests have been made, which show that the amount of new surface produced per revolution of a mill remains constant when grinding the same ore to different sizes and with different circulating loads.

Grinding-efficiency calculations on the basis of new surface area produced give results of about 60 per cent. However, they are subject to revision downward because of possible errors in the surface energy, as measured by the pendulum impact device.

Efficiency calculations based upon either mesh sizes or surface areas are apt to be misleading. The *unlocking* efficiency, which at present is an indeterminate quantity, is the correct measure of efficiency in ore grinding.

## References

1. W. L. Maxson, F. Cadena and F. C. Bond: Grindability of Various Ores. *Trans.* A.I.M.E. (1933) **112,** 130.
2. F. C. Bond and W. L. Maxson: Crushing and Grinding Characteristics Determined from Screen Analyses. *Trans.* A.I.M.E. (1934) **112,** 146.
3. R. Wilson: A Method for Estimating the Efficiency of Pulverizers. *Trans.* A.I.M.E. (1938) **129,** 170.
4. S. D. Michaelson, J. M. Wolf and W. L. Maxson: Grindability of Various Ores as Affected by Circulating Loads. Presented at A.I.M.E. New York meeting, February 1936. Unpublished.

## DISCUSSION

(*T. B. Counselman presiding*)

O. C. Shepard,* Stanford University, Calif.—In 1929 the Bureau of Mines reported tests at the Tooele and Midvale mills in Utah[5] in which the total grinding efficiency was about 65 per cent, considering power input and the power represented in the new surface produced. This seems to check well with the results given by Bond and Maxson.

Useful efficiency was also investigated.[5] It was based on the assumption that the minerals broke free at a certain size, and that grinding finer than that size was useless, which gave a useful grinding efficiency of only about 5 per cent. Of course, there is not complete unlocking of mineral grains at any one mesh size, but the results do show that while there is fairly good efficiency in total grinding, there is still something to strive for in raising the efficiency of grinding to unlock the minerals.

W. L. Maxson.—Possibly there is more hope than was held forth a few years ago in that respect. At least apparently we are increasing somewhat the efficiency and capacity of grinding circuits. That "we" is a very inclusive term, because everyone that is interested in grinding, including the operators, and, I think, the equipment manufacturers, has helped. I believe some real advances have been made.

T. B. Counselman,† Chicago, Ill.—The principal question seems to be the accuracy of the power measurements of the pendulum test, and Mr. Maxson has pointed out that by using alloys of varying hardness different figures are obtained, and therefore that must be taken into consideration. I know that Mr. Coghill, of the Bureau of Mines, worked for about two years on drop tests to find a real power input into crushing, and he told me three or four months ago that he had given it up because he could not correlate his results; they were too erratic.

W. L. Maxson.—Yes, we found that to be true.

T. B. Counselman.—The part of the paper on "correction and screen analyses" describes a method that should be used frequently, because screen analyses are apt to be erratic. The only trouble that I see with the method given for working out grinding efficiencies is the immense amount of work involved. Some of us would get lost in these calculations.

W. L. Maxson.—We have tried to simplify the method and make it as clear as possible, but, after all, there is a point beyond which no more can be done.

---

* Associate Professor, Mining and Metallurgy, Stanford University.

[5] Efficiency of Grinding Mills. U. S. Bur. Mines *R. I.* 2952 (1929).

† The Dorr Company, Inc.

Of course we are using a machine that is rather definitely established in the testing of steels. We use for our small test pieces a steel that has been heat-treated and normalized, and which always has the same structure. For any given comparative tests we can get that section down to a point where the repeated checks are plus and minus 1 to 2 per cent on the breaking strength, so that we feel that, having tested so many different materials and being able to get repeat checks, this may offer a little more accurate method—at least from the standpoint of being able to check oneself—than the drop-weight methods.

T. B. Counselman.—Don't you think, Mr. Maxson, that the point is right there—that you carried out this test on a certain empirical procedure each time? For example, you load a cyclinder with a certain weight of material of varying sizes, so I should think it would make a tremendous amount of difference how firmly that material is packed.

W. L. Maxson.—Yes, it is necessary to standardize operations. The material is placed in the tube and is shaken a certain number of times and is tapped a certain, definite number of times. We compact it by shaking.

T. B. Counselman.—Do you think that is a more accurate way of getting empirical results than, if it were possible to do so, by taking an individual grain and placing between striking blocks?

W. L. Maxson.—We have done a great deal of work on deformation of individual pieces—larger pieces, of course. The work has been done with a pressure machine with a load applied at various rates and with various shapes and sizes. We have worked with both cubes and cylinders, and the ratio of diameter and length has been changed. We have not found that the work with larger pieces can be at all concordant—there is a great deal of difference in the way such pieces split and shatter off.

T. B. Counselman.—That is the point. It is almost necessary to adopt an empirical procedure and be satisfied with it, because the shapes of all the little pieces vary so much; little corners and fragments are apt to break off and change the results. The base line of observation must be spread out long enough to try to eliminate or average all potential errors.

W. L. Maxson.—One interesting thing has been brought out by the tests, both on ore and synthetic samples—that is, the breaking under pressure almost always results in the formation of tetrahedrons, regardless of crystalline structure. The general tendency with coherent material that is not, we will say, needlelike, is to form tetrahedrons. That is interesting because apparently it checks back pretty well with some of the work that has been done on subsidence. We have made a specific mathematical analysis to determine the reason for this, and find that when pressure is applied on a cylinder the cracks go up around the cylinder more or less in spirals, and the end is a sort of rough tetrahedron. It may have a concave face, but its general shape is tetrahedral.

T. B. Counselman.—When you mudcap a boulder, you get a tetrahedron nearly every time.

W. L. Maxson.—This may seem involved from the standpoint of practical mill men, but after all, in any kind of a grinding mill, eventually the action comes down to contact between two balls and the particles between them. We have tried to simplify to secure a better understanding of what exactly takes place in a mill. We have tried to express it in terms of a simple fundamental, a single sphere, or a single cylinder.

The more one works with this particular subject, the more one develops a sense of humility, because it is much more complicated than is generally recognized.

MEMBER.—The amount of revolution of a mill remains constant to different sizes of different circulating loads. Have any conclusions been reached on the question of larger and smaller circulating loads?

W. L. MAXSON.—That was brought out at a previous meeting.[6] We have been doing some testing to determine optimum circulation; in other words, the critical circulating loads. Apparently there is a critical circulating load, but it appears to vary with different ores and different meshes in the same ore. In other words, in grinding different ores to the same mesh, there will be a different optimum in the circulating load. This must not be forgotten in talking about circulating loads, and I think it is often overlooked. For example, in the gold industry, people are prone to criticize modern classifiers and say that they do not make a clean sand, and return too much unfinished material to the mill. Looking at it from the standpoint of screen analysis, that is true, but from the standpoint of metallurgical efficiency, it is not true; the classifier separates not only according to size, but also according to specific gravity. For instance, in cyaniding, where the sulphides tend to segregate in the sand, we get grinding on the sulphides (the heavier part of the ore) and thus secure exposure necessary to make an attack by cyanide possible, so that when we talk about circulating loads we must, perforce, tie that down to the definite job under consideration. It is difficult to generalize on such a subject.

MEMBER.—I suppose a critical mill speed would follow?

W. L. MAXSON.—Critical mill speed, critical ball size, and critical density are interdependent factors.

It has been interesting to note, when running a series of simple closed-circuit tests for a given ore, that there is apparently a hump in the curve of maximum production, and in a few cases that we have checked in the field it seems to check out very closely. For example, at New Cornelia the maximum circulating load seems to check fairly closely with the optimum figure given on page 311. I have interpolated figures of other mesh sizes. For instance, in Table 4 at 65 mesh there are tests at 250 per cent circulating loads and 150, 400, and 800 per cent loads. While there is an increased production up to 800 per cent circulating load, the net increase above 400 per cent is meager. That checks fairly well with practice. The last time I was there they were running about 470. We have run some tests in between at 500 and 600 but there appears to be some circulating load beyond which only more mechanical difficulties are introduced and there is not enough gain in grinding capacity to pay for it. It is possible roughly to evaluate whether a big circulating load or a small one should be used.

MEMBER.—In getting a proper ball size for petroleum coke, have you ever used cubes?

W. L. MAXSON.—Yes, we have used tetrahedrons and cubes and cylinders in which the diameters are roughly equal and the length is one and one-half times the diameter. We are not able to show any gain by using cubes or tetrahedrons. The best results on a material like petroleum coke can be secured by an impact machine.

A. F. TAGGART,* New York, N. Y.—Did you make any determination as to possible differences in size of the minus 200-mesh material with different sizes of feed to the cylinder in the impact tests? I had an idea a number of years ago that one could reverse the Bureau of Mines' sand detonator test in order to determine the extent of crushing. General theory underlying this idea was that the detonator test showed that detonators expended a reasonably constant amount of power and that if, therefore, one took different sizes of feed and expended these given amounts of power on them the effects on different feeds of a constant power input could be determined. But I found that I got distinctly different distributions of sizes in the minus 200-mesh products, according to the sizes fed; i.e., whether minus 14, plus 28-mesh, or minus 48, plus 65, or a composite sample that had a certain amount of minus 14 and a certain amount of minus 28, and so forth.

---

[6] Ball Milling. *Trans.* A.I.M.E. (1934) **112**, 60 et seq.

* Professor of Ore Dressing, School of Mines, Columbia University.

W. L. Maxson.—We have not tried it, but I think we shall do so now that you have raised the point.

T. B. Counselman.—I am interested in the reiterated statement in the paper as to the optimum circulating load for a given ore. It is obvious that different kinds of ores require different circulating loads, but to say that on a given ore there is an optimum circulating load and beyond that money is spent uselessly raises a question in my mind.

W. L. Maxson.—I think that is quite open to question.

T. B. Counselman.—For instance, at Braden some years ago a series of tests was carried out beginning with an open-circuit rod mill handling an initial feed of about 1000 tons and producing 315 tons of minus 100-mesh a day. They close-circuited that rod mill with one classifier, and step by step converted it into a ball mill and added more classification capacity, records being taken at each change, until finally they had a circulating load of about 11 to 1; and the production of minus 100-mesh per day from approximately the same initial feed, prepared in the same way, went steadily upward. There was no tendency, as far as tests of grinding capacity went, to show a stopping point. Most of the increase in capacity occurs in the first 100 per cent recirculated, and there does not seem to be any indication of a limit with larger circulating loads.

E. W. Davis,* Minneapolis, Minn.—I did some work in connection with ball mills when I was much younger and much bolder, and I wrote a paper for the Institute that I have been defending ever since.[7] However, our work showed that as we increased the circulating load the amount of material crushed to the desired mesh increased, but the rate of increase became slower as the load became larger. In those tests we used classifiers, and one thing I was never sure of was whether or not the change in classification efficiency as we increased the load was not in part responsible for the slight tendency of the increment of increase to become smaller.

T. B. Counselman.—You mean that was due to a decrease in classifying efficiency with the higher circulating loads?

E. W. Davis.—I am not sure whether that is correct or not.

T. B. Counselman.—In other words, if the classification figure had remained the same, do you think that the mill capacity would have gone more steadily upward?

E. W. Davis.—That is my reaction at the present time.

---

* Superintendent, Mines Experiment Station, University of Minnesota.

[7] E. W. Davis: Fine Crushing in Ball Mills. *Trans.* A.I.M.E. (1919) **61**, 250.

T. B. Counselman.—Mr. Maxson, that is apparently contrary to your theory of optimum circulating load.

W. L. Maxson.—No, I do not think it is really contrary. I have studied Mr. Davis' results very carefully from time to time during the last 10 or 15 years and I always considered that was a very fine contribution to our knowledge of grinding. We only did this work of ours to find out, if possible, what could actually take place in the mill between the balls which might produce more surface by moving material more rapidly between the balls.

If we disregard the classifier end of it altogether, we feel that, for a given mill at a given speed, and at a given density, to make a certain product, there is probably some critical flow rate through the mill. The only way today to control flow rate is to change the so-called circulating load. Whether that results in sweeping the mill to force out the finished material, which, of course, is the essential problem, is something that I do not know; but I suspect that there is probably the answer. What do you think about that, Mr. Davis?

E. W. Davis.—There are many variables to consider. In most of the tests I have seen a start was made with one set of conditions and the test proceeded with the change of only one variable. Perhaps we lose sight of the fact that as we build up the circulating loads other variables should be changed for best efficiency—the density of the pulp, the size of the balls and the mill speed. That, of course, makes the investigation spread out like the limbs of a tree, so I am not at all sure that we are justified in generalizing too much.

In addition to that, nowadays, many people are interested in selective grinding. They may wish to grind only the mineral or the gangue. All of this makes the problem more complicated.

W. L. Maxson.—In dry grinding, which of course is not the same as wet grinding because the close-circuiting may be done with air separators, or with screens, there is a definite circulation beyond which there is no gain.

T. B. Counselman.—Does that tie up with the efficiency of the separators?

W. L. Maxson.—It is more particularly true on the primary end, where we close-circuit with screens, say at 35 mesh. Apparently there is a very definite critical circulating load. I say definite; it is within 15 or 20 per cent. To go another 100 per cent beyond that gains nothing.

Grinding is one of the most expensive things in cyaniding or in concentration of any kind; it is one point where the expense is still high. Every operator is interested in some means of reducing that expense—that continual outpouring of money for grinding. If discussions of this kind—disregarding altogether the question of whether it should be a big circulation or a small circulation—will lead to a critical analysis of our problems to determine our own optimum conditions, I think we will have served some useful purpose.

C. H. Benedict,* Linden Lake, Mich.—Do I understand that with a series of ores, or just, say, two ores, and relative grinding efficiency and ease of grinding and so on, it follows the same throughout the different meshes?

W. L. Maxson.—No, it does not. We have ores that are extremely hard to grind in the coarse meshes, and some that are extremely hard to grind in fine meshes. One of the ores in northern Ontario has a distinct hump between 100 and 125 mesh.

---

* Metallurgist, Calumet and Hecla Consolidated Copper Co.

Microscopic analysis of the circulating load at one of these humps will usually reveal some distinct grain size, something that accumulates and is hard to break.

T. B. Counselman.—Mr. Davis made an interesting point about the possible necessity of changing the size of balls as the circulating load increases. I had an interesting experience a few years ago at a cement plant. Closed-circuit grinding had been put in on the wet end very successfully and the operators thought that all they had to do in the way of circulating loads was to increase production on the clinker end. They changed their clinker mills around so that one mill was used for coarse grinding with closed circuiting of the screens, and the tube mill was used for finishing. They expected to get somewhere around 100 or 150 per cent increase in the capacity of the mill, but obtained only 40 to 60 per cent increase. After a while somebody thought of changing the sizes of balls in the charge, and that overcame the difficulty.

W. L. Maxson.—That is a definite practice in the dry-grinding of cement. As the circulating load is increased the average size of ball must be increased, and the tendency is to increase it so much and use such large balls that there is not enough grinding surface.

E. W. Davis.—There is another point that should be mentioned. It is a simple matter to change the size of the balls in the mill, or the pulp density, but the manufacturer of ball mills should make it almost as easy to change the speed of the mill. I talked about this many years ago, but even now it is a major operation to reduce the speed of a mill by a half-revolution a minute.

W. L. Maxson.—What we should like to have, Mr. Davis, is some kind of power device that would give us the desired torque at any speed. Much work has been done on this but the only simple thing we can do at present is to put a direct-current motor on the mill.

There are plants with 20 or 40 ball mills all connected for a perfectly definite speed and no way to change progressively as the liners wear, which changes the inside diameter, and thus changes their efficiency. The one thing that would most radically affect the power consumption is a progressive change in speed, and that is not easily accomplished without changing the efficiency of the prime mover.

N. L. Shepard,* East St. Louis, Ill.—In the nonsulphide field, the Aluminum Ore Co. is operating a small flotation plant in Rosiclare, Ill., on a mixture of calcite, fluorspar and quartz. Two 3 by 5-ft. Hum-mer screens are used, with a circulating load of about 400 per cent, to make a separation at 65 mesh. A stainless-steel screen 60 by 42 mesh has been the standard, although at times a 70 by 32-mesh screen has been used for experimental purposes. The long opening is placed down the slope, which has varied from 20° to 28°. One screen is driven at 1800 r.p.m., while a frequency changer was installed to drive the other at 3600.

We have been bothered a good deal by blinding, so much so that our wear on the screens has been caused by the steel brush that the operator uses for cleaning. We often consider going back to classifiers. We desire material that is all minus 65 mesh with a minimum of minus 325 mesh. We now produce about 25 per cent minus 325. If we can get that down to 12 per cent minus 325 we will be satisfied.

W. L. Maxson.—We have done some work on wet screens with more or less the same problem in mind that you have, where great trouble is experienced because the shapes of the particles cause blinding of the screens. We have found that if the screen is operated submerged it is possible to get good capacities without blinding. That means, of course, a rather special type of screen. If you can so arrange your screens that you submerge them under water so that the material delivers out above the water level, it is possible to secure higher capacities. The sized distribution under those conditions is close to the limiting mesh. As the circulating load is increased, the size distribution approaches more closely the limiting mesh.

---

* Research Chemist, Aluminum Research Laboratories, Aluminum Ore Co.

The question of size distribution is less important in the mining industry, but in nonmetallics it is extremely important. A good example is Norris Dam, where a very large saving was made in the amount of cement required by the use of a proper-size modulus in the aggregates.

The Reclamation Service has worked intensively on that problem. The present tendency in the preparation of raw materials for the larger projects, where there is a large amount of cement involved, is to secure a modulus of suitable size. Size modulus presupposes controlled void space in the aggregate. That leads to a careful study as to how material can be treated to give close distribution of sizes.

F. C. Bond and W. L. Maxson (written discussion).—It is generally appreciated that the most important advances in our knowledge of the comminution of materials lies in the exploration and development of the underlying fundamental laws, rather than in the accumulation of more empirical data. Until these fundamentals are fully explored there can be no real standard of efficiency, and wasteful installations are to be expected. Probably the most significant part of our paper is that which deals with the total amount of work done in grinding. All of our data tend to show that, under the different grinding conditions investigated, a given amount of power input resulted in the production of an equivalent amount of new surface area. In other words, changes in the grinding conditions, such as circulating load, ball size, and mill speed, may greatly increase the efficiency of grinding to all through a certain mesh size, but do not affect the amount of new surface area produced. Considerable experimental work done since the publication of the paper supports this conclusion.

The relationship may be expressed mathematically as

$$\frac{K \times \text{Power Input to Material}}{\text{Surface Energy of Material}} = \text{New Surface Area}$$

where $K$ is a constant quantity.

It is certainly worthy of serious consideration in connection with crushing and grinding phenomena.

# Magnetite as a Standard Material for Measuring Grinding Efficiency*

By R. S. Dean,† Member A.I.M.E.

(New York Meeting, February, 1936)

The careful work of Gross and Zimmerley[1] has established the fact that the energy actually used in grinding is proportional to the new surface produced. This confirmation of Rittinger's law was made by crushing quartz in a frictionless drop-weight machine and determining the surface of the quartz by its rate of solution in hydrofluoric acid. The details of this procedure have been described adequately elsewhere and need not be repeated here. The resultant data furnish the only available basis for comparing accurately the efficiency of grinding machines.

This method is so cumbersome experimentally that it has been little used. As an alternative all sorts of approximations have been proposed. The best of these is complete size analysis by sieving and elutriation. Such procedure is very lengthy and difficult to carry out accurately. Furthermore, any sizing method becomes very inaccurate for determining surface with very fine sizes where the ratio of surface to volume becomes very large. To avoid the lengthy and difficult technique of elutriation it has been proposed to estimate the size distribution below 200 mesh from various probability formulas. Such a procedure is at best an engineering approximation; at worst it is a mere guess.

Some time ago Dr. V. H. Gottschalk[2] found that the coercive forces of magnetite powders were directly proportional to the surface area, regardless of size distribution. It was at once apparent that this furnished a method for determining grinding efficiency quickly and accurately. The only requirement was a single determination of the relation between the work input of the Gross-Zimmerley drop-weight machine and the coercive force of the resultant crushed magnetite.

For this purpose Ural Mountain magnetite in definite octahedra was

---

* Published by permission of the Director, U. S. Bureau of Mines. Manuscript received at the office of the Institute July 30, 1935. Issued as T.P. 660, January, 1936.

† Chief Engineer, Metallurgical Division, U. S. Bureau of Mines, Washington, D. C.

[1] J. Gross, S. R. Zimmerley and S. J. Swainson: Surface Measurement on Finely Ground Particles and Its Relationship to the Crushing Laws. Univ. of Utah *Bull.* (August, 1925) **16**, 57–76.

[2] V. H. Gottschalk: The Coercive Force of Magnetite Powders. U. S. Bur. Mines *R.I.* 3268 (1935) 83–90; *Physics* (1935) **6**, 127–132.

selected and given a preliminary crushing through 10 mesh. Gross then prepared 16 samples by crushing in the drop-weight machine, increasing the work input on each succeeding sample. The resulting magnetite powders were then used for coercive-force measurements. These measurements were made in Dr. Gottschalk's laboratory by a new method developed by C. W. Davis, of that laboratory. The results of this work are shown in Table 1 and Fig. 1. This clear-cut linear relationship between work input and increased coercive force is a striking confirmation of the generality of the original Gross-Zimmerley surface-work relationship as well as of Gottschalk's surface-coercive force relationship.

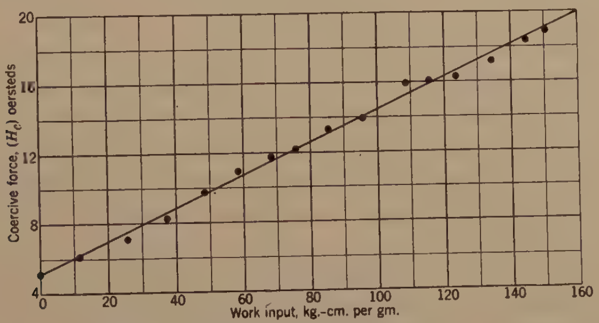


Fig. 1.—Relation of coercive force and work input for crushing Ural Mountain magnetite.

Table 1.—*Relation of Coercive Force and Work Input for Crushing Ural Mountain Magnetite*

| Sample No. | Coercive Force, Oersteds | Work Input per Gram, Kilogram-centimeters | Sample No. | Coercive Force, Oersteds | Work Input per Gram, Kilogram-centimeters |
|---|---|---|---|---|---|
| 1 | 5.12 | 0.0 | 9 | 13.34 | 85.2 |
| 2 | 6.1 | 11.4 | 10 | 13.98 | 95.4 |
| 3 | 7.06 | 25.9 | 11 | 15.89 | 108.6 |
| 4 | 8.22 | 37.6 | 12 | 16.02 | 115.2 |
| 5 | 9.74 | 48.3 | 13 | 16.3 | 123.9 |
| 6 | 10.94 | 58.5 | 14 | 17.21 | 134.8 |
| 7 | 11.77 | 68.5 | 15 | 18.38 | 144.4 |
| 8 | 12.18 | 75.7 | 16 | 18.94 | 150.3 |

The practical importance of these data is evident. Magnetite is a cheap and readily available material of medium hardness and therefore is well suited to comparison of grinding machines. To determine machine efficiency it is only necessary to charge the machine with 10-mesh magnetite and note the power input on a watt-hour meter or by other means while grinding. After the magnetite is ground a representative sample is taken, the coercive force is determined, and the actual work input is read from Fig. 1 (corrected for the coercive force of the massive magnetite).

Coercive force can be determined by the Davis method in a few minutes. The method will be described in detail elsewhere[3]. A brief description will serve to show its simplicity.

The crushed sample in a suitable container is thrust momentarily into a magnetizing coil. It is then placed at the center of a long horizontal primary solenoid in such a direction that when a current is passed a magnetic field opposing that of the sample is produced. When the sample is moved suddenly along the common axis of the primary solenoid and of an enclosing secondary coil attached to a galvanometer, a deflection is observed unless the two fields are exactly balanced. When a balance has been established the field intensity of the primary solenoid gives a direct measure of the coercive force ($_IH_c$).

Magnetites may vary slightly in their coercive force-surface relationship, but in general the variation will not be large enough to affect seriously the results. In the near future we hope to standardize the method for several of the larger sources of domestic magnetite.

---

[3] C. W. Davis and M. Hartenheim: A Simple Method for the Determination of Coercive Force. *Review of Scientific Instruments* (March, 1936) **7**, 147–149.

# Rod-mill Practice at Ray Mines Division, Kennecott Copper Corporation

By F. J. Tuck*

(Tucson Meeting, November, 1938)

The Hayden mill of the Ray Mines Division, Kennecott Copper Corporation, is now equipped with two 9 by 12-ft. rod mills having a daily capacity of 6000 tons of coarse-crushing plant product from the mine. These two mills crush a ¾-in. product to approximately 19 per cent on 14 mesh, with only one pass through the mills. Each rod mill has taken the place of four sets of 42-in. Garfield rolls with their attendant screens, and is making a product for the fine-grinding department comparable to that formerly made by rolls in closed circuit with screens.

The rod mills are lined with wave-type liners of white iron, varying in thickness from 2 to 3 in. The shell and end liners last approximately 600 to 700 days. Manganese-steel lifter bars, 3⅝ in. thick, are used, spaced about 11 in. apart, and they give a life of 350 to 450 days. Fig. 1 shows the general design and thickness of the wave-type liners and lifter bars; 1½-in. liner bolts are used to fasten the lifter bars to the shell. The shell liners are held in place by the tapered lifter bars. A ¾-in. wood backing is used between the shell and the liners.

The rod-mill scoop has removable manganese-steel lips, which last 250 to 300 days. The scoop proper has shown some wear in spots, and these spots have been protected by rubber bolted over them.

Water and milk of lime are added to the elevator feeding the mill, but not enough water to cause a pounding of the rods against the shell. Roughly, the water added amounts to 25 to 33 per cent of the ore. Additional water is added to the mill discharge to facilitate distribution to the classifier bowls in the fine-grinding department.

Rods are charged to the mill once every four days, the mill being down about 20 min. for this purpose. Other delays are negligible, and usually are due to a loose liner bolt or possibly power trouble. However, these occasions are extremely rare. In charging the mill, a crane is used

---

Manuscript received at the office of the Institute Aug. 2, 1938. Issued as T.P. 994 in Mining Technology, November, 1938.

* Assistant Mill Superintendent, Ray Mines Division, Kennecott Copper Corporation, Hayden, Arizona.

to handle the rods, which are wired in bundles of eight each. The wire is cut after the rods are in place in the mill. It is worthy of note that there is no tangling up of the rods during operation. They remain in alignment and wear down to a flat or lens shape, and are discharged from the mill in short pieces varying from 6 to 15 in. in length. Grids placed in the launders prevent the rods from reaching the fine-grinding department. The smaller pieces, which work through the grids, are caught in the center of the main distributing tub, or occasionally are removed by the operator. The reject amounts to about 4 per cent of the original rod charge.

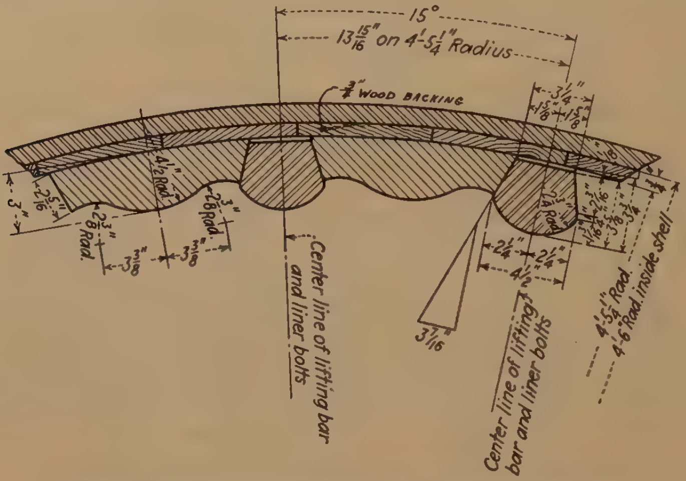


Fig. 1.—Part section of lifting bars and liners.

Table 1.—*Typical Sizing Test of Rod-mill Feed and Product*

| Mesh or Opening | Feed to Rod Mill Per Cent Material | | Rod-mill Product Per Cent Material | |
|---|---|---|---|---|
| | Orig. | Cum. | Orig. | Cum. |
| Inches: | | | | |
| On 0.742 | 3.92 | 3.92 | | |
| On 0.525 | 11.95 | 15.87 | | |
| On 0.371 | 11.76 | 27.63 | | |
| Mesh: | | | | |
| On 14 | 38.61 | 62.24 | 19.11 | 19.11 |
| On 65 | 13.74 | 79.98 | 36.78 | 55.89 |
| On 100 | 1.86 | 81.84 | 4.57 | 60.46 |
| On 200 | 2.60 | 84.44 | 6.25 | 66.71 |
| Through 200 | 15.56 | 100.00 | 33.29 | 100.00 |

Before a mill is started, the crane is used to back up the mill a part of a revolution, which loosens the rods and permits an easier start. The motor driving the mill is a 350-hp., squirrel-cage induction motor, 440 volts, 60 cycle, three phase, 435 r.p.m. Maximum starting torque is 200 per cent of full load torque, the motor being started on full voltage. Button switches are used in starting all machines, and each machine is automatically protected against operation of machines ahead of it. For instance, the elevator feeding the rod mill cannot operate unless the mill is running; the conveyor feeding the elevator is likewise protected against starting if the elevator is not running; and the feeders cannot start unless the conveyor is running.

A 22-in. leather belt, 48 ft. 6 in. long, connects the motor with the pulley driving the mill through a Wuest pinion and gear. An idler is used to give the belt a larger arc of contact on the pulleys. Other pertinent statistics covering the installation are as follows:

| | |
|---|---|
| Weight of mill with bearing bases, gear and pinion, 48-in. double scoop, and feed and discharge trunnion liners, lb. | 85,000 |
| Weight of shell liners, lb. | 22,800 |
| Weight of end liners, lb. | 4,100 |
| Weight of lifter bars, lb. | 12,000 |
| Weight of rod load, lb. | 80,000–90,000 |
| Rods, 3 by 11 ft. 4 in., 0.90 to 1.05 per cent carbon, hot-rolled, hot-sawed and machine-straightened, approximate weight each rod, lb. | 275 |

Speed of mill, slightly less than 14 r.p.m.
Average kilowatt-hours per ton ore milled, 2.08
Average pounds of rods consumed per ton ore milled, 0.38

The cost of fine crushing by rod mills is averaging about 5½¢ per ton. This includes power, steel, other supplies, shop labor, operating and repair labor, the complete cost of operating and maintaining, for each mill, four feeders, two conveyors, one bucket elevator and launders to and from the rod mill, and the regular allocation of operating overhead charges. This compares with 8¢ per ton during the best roll-crushing conditions.

## DISCUSSION

*(Guy H. Ruggles presiding)*

C. G. McLachlan,* Noranda, Quebec.—Discussion as to the merits of different crushing and grinding flowsheets that is not supported by figures showing costs in terms of actual surface produced is not of very great value. Mr. Tuck has furnished sufficient data in his paper to permit the cost of producing a unit of surface area to be calculated for the Hayden rod-mill operation.[1]

---

* Noranda Mines Limited.

[1] W. H. Coghill: Evaluating Grinding Efficiency by Graphical Methods. *Eng. and Min. Jnl.* (1928) **126**, 931–938.

The use to which the rod mill is being placed at Hayden is complementary to that of the ball mill. As a result, the arguments previously advanced regarding the advantages of rod milling vs. ball milling, and vice versa, do not apply, and in the present instance we are concerned directly with the economic breakpoint at which dry crushing should stop and wet grinding begin. For this particular instance the problem can also be restated as follows: Is it cheaper for dry crushing to be carried far enough to reduce the ore to the point where it can be fed directly to a ball mill, or should the ore be reduced only to a diameter of about 0.75 in. and then fed to a rod mill for reduction to ball-mill size?

As already stated, the cost of producing a unit of surface area can be calculated from the data given in the Hayden paper, and it seems to me that the next move is for the supporters of dry crushing to show that with an up-to-date crushing flowsheet they can accomplish the same result at a lower cost. In making this statement, I realize that the objection will be raised that, as ores have different characteristics, it is not fair to take figures for a fine-crushing operation at another plant and compare them with the Hayden rod-mill operation. Such an objection is valid, but I see no reason why figures cannot be obtained from different plants to show the relative costs of crushing and grinding, in terms of surface formed at each plant. Naturally, no definite conclusions could be drawn from any single set of plant results, but if it were shown that the cost of producing useful surface in a wet-grinding mill is lower than that obtained, on the average, in a fine dry-crushing unit, I believe we would have to revise our present ideas as to the economic breaking point between crushing and grinding. Such a revision would not only have a direct bearing on operating costs but also on plant design.

# Improvements in Fine Grinding and Classification at the Hollinger Consolidated Gold Mines Ltd.

By H. W. Hitzrot,* Member A.I.M.E.

(New York Meeting, February, 1939)

The new 4800-ton fine-grinding plant at the Hollinger Consolidated Gold Mines property at Timmins, in the Porcupine district of northern Ontario, went into operation in November 1937, and represents the culmination of an experimental program.

The plant is a moderately low rectangular building of hollow tile on a steel frame, large enough to house four 7 by 15-ft. ball mills, with a 12 by 27-ft. classifier beside each mill. At one end is space for the addition of another mill and classifier or a mill and classifier for the regrinding of table concentrates. This regrinding is now done in the old grinding department of the main mill building. Also within the new building are the four 6-in. sand pumps for lifting the product from the low-discharge ball mills up to the classifier feed launders and the containers and appurtenances of a complete dust-collecting system. Together with the usual overhead crane, these constitute the major units of equipment within the new plant.

The location is at the lower end of the main mill buildings toward the old tailings pond, now so neatly leveled off and sodded to rival the very best of our own W.P.A. projects. Close by the new grinding plant is a large dome-shaped structure—the new fine-ore bin designed and built by Mr. Longmore and the Hollinger milling and engineering staffs. There are four separate automatically loaded inclined belt conveyors leading up from the bottom of the bin to the grinding plant. Each belt is equipped with a recording weightometer, in the grinding building. The whole structure and the machinery within it give the impression of permanence and a carefully integrated design with close attention to details, giving the operators every advantage for consistently good work.

The many ideas and opinions behind this achievement were all ably organized and executed by the Hollinger milling and engineering staffs, and not a few were directly initiated by them. Excellent cooperation was afforded by the Hollinger staff to the engineers helping to conduct

---

Manuscript received at office of the Institute March 8, 1939. Issued as T.P. 1088 in Mining Technology, July, 1939.

* Metallurgical Engineer, The Dorr Company, Inc., New York, N. Y.

the grinding and classification test program. It was the author's privilege and good fortune to be, almost from its inception, intimately associated with the many phases of this grinding and classification modernization program.

## Fine Grinding and Classification Practice Prior to Modernization

The test program was carried on from 1934 to 1936. Before that time the normal grinding and classification operation in the Hollinger mill was along a well-established method. The 4800 tons per day of ore crushed to minus ¾ in. was fed by electrically controlled roll-type bin feeders to five 7 by 15-ft. Marcy rod mills, a sixth unit being used part time to make up the additional tonnage required and as a spare unit. Each mill was capable of handling about 950 tons, on the average. The discharge from each rod mill flowed by gravity down through about a 10-in. pipe some 30 to 40 ft. long into a short length of rectangular steel trough at the end of which was a vertical wedge splitter. The rod-mill discharge was thus divided into two 6 by 29-ft. model D Dorr classifiers, each in closed circuit with a 6 by 16-ft. Fraser and Chalmers pebble mill charged with 4-in. flint pebbles, imported from Belgium. The classifier overflow from the secondary circuit normally was 2 to 4 per cent plus 48 mesh and 60 to 65 per cent minus 200 mesh, and about 39 to 40 per cent solids. After dilution with cyanide solution to reduce the solids to about 26 per cent, it was laundered to the various rotary distributors in the succeeding vibrating-table section. Incidentally, all grinding and classification operations were and are still carried on with the normal weak cyanide solutions having the small amount of burned lime for protective alkalinity added at the crushing plant.

Fig. 1*a* represents one section of the long-established Hollinger grinding circuit. Operating five such sections with a sixth running part time, some commendable grinding cost figures had been attained. The Hollinger ore would be classed as only moderately hard, as it contains some relatively soft and friable schist, but there is a large amount of quartzite, which is hard and tough. Some 4 to 6 per cent of sulphide is present in the ore and this is practically all removed by the table operation. The concentrate from the tables is given a separate treatment, being ground to about 98.5 per cent minus 200 mesh and separately agitated before it joins the main countercurrent cyanide circuit.

## Important Investigations Affecting Changes

In the early spring of 1934 an attempt was made to reduce the amount of plus 48 mesh and tramp oversize in the overflow from the 6-ft. model D classifiers in the secondary circuit. A baffle that had been recently designed for the pool end of the classifier was used for the purpose. Although no improvement in the classifier overflow was effected by this particular change, some other interesting information was gleaned. It was demonstrated that the efficiency of the classification was improved

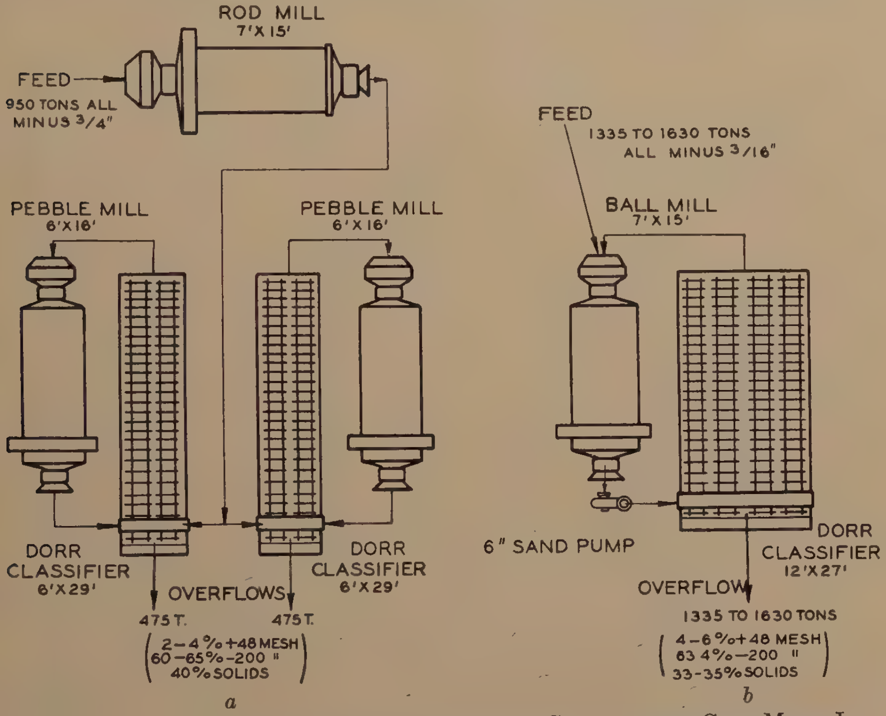


FIG. 1.—TYPICAL GRINDING SECTIONS AT HOLLINGER CONSOLIDATED GOLD MINES LTD. *a*, old grinding plant; *b*, new grinding plant.

*Comparative Operating Data*

| | Old Plant | New Plant |
|---|---|---|
| Total power consumption, hp: | | |
| Rod mill | 225 | |
| Ball mill and classifier | | 384–472 |
| Two pebble mills and classifier | 254 | |
| Sand pump | | 23–28 |
| Total | 479 | 407–500 |
| Unit power consumption: | | |
| Horsepower-hours per ton ground | 12.10 | 7.32–7.36 |
| Kilowatt-hours per ton ground | 9.03 | 5.46–5.49 |
| Minus 200-mesh balance: | | |
| Percentage in feed | 13 | 15.3 |
| Percentage in overflow | 62.5 | 63.4 |
| Tons produced | 470.0 | 721.5* |
| Horsepower consumed per ton | 1.02 | 0.63–0.46 |
| Total cost crushing and grinding: | | |
| Cents per ton | 21.26 | 17.93 |

* At 1500-ton rate.

and a reduction in the amount of tramp oversize in the overflow was obtained when the classifiers were speeded up from 23 to 30 strokes per minute and the solids in the overflow were reduced to 37 to 38 per cent from 40 to 41 per cent.

The pebble mills had a decidedly limited circulating-load capacity—they soon overloaded and the mass choked the discharge grate—but with better classification and elimination of finished material in the overflow more new feed could be added to the section and each section was able to handle some 50 to 75 tons more feed, so that each section could grind 1000 to 1025 tons instead of 950.

It became evident early in the investigation that the bottle neck of the circuit was the pebble mills. Considerable time was spent by the Hollinger staff investigating steel balls for the secondary mills. As the 6 by 16-ft. pebble mills were thought to be too light in construction for a steel ball charge, an available 5 by 20-ft. tube mill was used and loaded with steel balls. This mill was also in closed circuit with a 6 by 29-ft. model D classifier. The 5 by 20-ft. ball mill handled about 700 tons, as against about 475 for the 6 by 16-ft. pebble mill. Also, it was indicated that the ultimate grinding capacity of the mill had not been reached. The limiting factor in this case was the sand-raking capacity of the 6-ft. wide model D. Some deeper rake blades were tried by the Hollinger staff in an attempt to increase the raking capacity, but with only indifferent success. As the progress was studied at this point particularly from the standpoint of the secondary mill loaded with steel balls, there were indications that further progress could be made with a classifier of sufficient sand-raking capacity to keep an adequate load circulating around through the mill and so improve grinding costs.

## Experimental Section in Grinding Department of Old Mill

Concurrent with the decision to conduct a modern large-scale grinding test was the decision to use one of the 7 by 15-ft. rod mills for the test program. An order was placed for a heavy-duty Dorr model FX classifier 12 ft. wide by 27 ft. long, having quadruplex rakes. The decision to use the rod mills in preference to either the pebble or the tube mills was logical in that they were newer mills and constructed to offer the greatest latitude of operating possibilities.

In November 1935 the mill and classifier were set up and ready to commence the tests. For the initial work the mill remained as a rod mill running at 16.2 r.p.m. and driven by a 225-hp. motor. The FX classifier was set up on a steel framework directly above and over the mill so that the rake sands flowed by gravity into the scoop box. The classifier overflow also ran by gravity and joined the main flow of pulp to the table distribution boxes. The mill discharge flowed down directly into an available 10-in. Morris sand pump on a lower floor, which pumped it up through a 12-in. wood-stave pipe into the classifier feed box. At first the mill discharge ran into a concrete pump box but after this box had filled up on several occasions, probably because the pump was oversize and became air-bound, the box was by-passed and mill discharge was run directly into the pump suction connection.

A very important consideration in this or any similar large-scale grinding test is the mill-feed scoop. An error was made in the design of the scoop first used and a delay of several days was required while an entirely new scoop of correct design was made in the Hollinger shops. This is a two-way (double) scoop 72 in. in diameter with an opening 16 in. wide. It functioned very satisfactorily on the test section and is performing equally well on each of the four ball mills in the new plant.

As mentioned, tests were started with the rod mill, which had been receiving the normal charge of 3-in. diameter rods. No exhaustive test was conducted under these conditions as it was soon discovered that with a normal load of rods the average tonnage that could be ground to the required fineness was around 470 tons per 24 hr. Also, it was observed in this and subsequent tests using rods that the classifier became loaded with a highly granular mass, within an inch or two of the weir level, so that in milling parlance only "dirty water" overflowed from the classifier.

Next a test was run with additional 3-in. rods added to bring the steel load up 4 to 6 in., but no substantial benefit was observed.

Another test was run after removing all of the plus 2-in. rods and replacing them with 2-in. rods. Some increase in the tonnage ground was effected, especially when the rod load was brought up to approximately the center line of the mill. Perhaps it is safe to say that 590 tons could be averaged under these conditions, but there were several features apparent, such as lack of slimes in the mill discharge and consequent pumping of a highly granular product, that made the circuit difficult to control.

Although it was reasonably well known beforehand that a mill 7 by 15 ft. would handle more tonnage as a ball mill than as a rod mill, the Hollinger staff wished to investigate the possibilities of a rod mill in closed circuit with the heavy-duty FX classifier. The next logical step in the progression naturally was the ball mill.

The mill speed was first increased to 22 r.p.m. and a 300-hp. motor replaced the 225-hp. unit. After several weeks of operation under these conditions, the mill speed was raised to 24.5 r.p.m. and the 300-hp. motor was replaced by a 350-hp. unit (actually 400 hp.). The door of the rod mill was removed and the 21-in. diameter opening was covered with an outside ring grizzly 21-in. diameter by 2 ft. long with ½-in. opening. The mill measured 6 ft. 6 in. by 14 ft. 6 in. inside the liners, was supported on four rollers and, therefore, had no trunnions, and had a 14-in. diameter throat opening into the mill through a neck 12 in. long. The feed scoop was a 72-in. diameter double-acting type 16 in. wide at the tip opening. The ball charge was made up of 14.3 tons 3-in., 14.3 tons 2-in. and 5.0 tons 1⅝-in., making a total of 33.6 tons, which brought the load up to center line. The large Morris sand pump for elevating the mill discharge to the classifier was replaced by a 6-in. Morris sand pump.

TABLE 1.—*Costs*

On Tonnage of Approximately 5000 Tons per 24 Hours

| Operation | Year | Cost per Ton |
|---|---|---|
| Rod milling | 1931 | $0.0741 |
| | 1932 | 0.0735 |
| | 1933 | 0.0732 |
| | 1934 | 0.0701 |
| | Average | 0.0727 |
| Tube milling (using flint pebbles) | 1931 | 0.0659 |
| | 1932 | 0.0618 |
| | 1933 | 0.0607 |
| | 1934 | 0.0566 |
| | Average | 0.0613 |
| Total[a] | 1931 | 0.1602 |
| Total[a] | 1932 | 0.1539 |
| Total[a] | 1933 | 0.1522 |
| Total[a] | 1934 | 0.1458 |
| Total[a] | Average | 0.1530 |
| Classification average for the four years | | 0.0098 |
| Crushing[b] | 1931 | 0.0584 |
| | 1932 | 0.0583 |
| | 1933 | 0.0634 |
| | 1934 | 0.0581 |
| | Average | 0.0596 |

[a] Total grinding cost, including rod mills, feeders and conveyors, spill collection, tube milling, classification, screw conveyors and clean-up under tube mills and classifiers.

[b] Crushing during this period consisted of primary and secondary gyratories followed by rolls in closed circuit with trommels having punched-plate screens.

A detailed account of the test work done during the next 12 months and a log of the performance of the ball mill with its heavy-duty classifier were given in a paper prepared by the Hollinger mill staff.[1] In closed circuit with the 12 by 27-ft. FX classifier, the 6-ft. 2-in. by 14-ft. 6-in. test ball mill operating with a circulating load ratio of between 5 and 5.5:1, charged with 3-in. balls, with smooth liners and a low discharge handling 1430 tons per day to a reported 2 per cent plus 48 mesh and 66 per cent minus 200 mesh was run with the following estimated cost: crushing, 6.50¢ per ton; ball-milling and classification, 11.12¢ per ton; total, 17.62¢ per ton. Compare this with the cost for the four years 1931 to 1934, as shown in Table 1; that is, crushing 5.96¢ per ton; total grinding, 15.30¢ per ton; total, 21.26¢ per ton.

---

[1] Comparison of Low vs. High Discharge for Ball Mills. *Trans.* Canadian Inst. Min. and Met. (1937) **40**, 85–109.

A supplementary paper was written by the Hollinger mill staff bearing the date of March 10, 1937, in which it was said that some 77 more tons per 24 hr. was ground by the low-discharge ball-mill unit with its heavy-duty classifier when 2½-in. balls were used instead of 3-in. This then brings the total average daily tonnage ground to 2 per cent on 48 mesh and 66 per cent minus 200 mesh up to 1507 tons. Incidentally, 1500 tons per grinding unit is the commonly accepted tonnage for the new grinding plant.

It will be noted that the crushing cost is 0.54¢ per ton higher in single-stage grinding than in the four-year average under the old system of open-circuit rod mills and secondary pebble mills. Even before the decision was made to proceed with the large-scale grinding test, the Hollinger mill staff began experimenting with finer crushing. There were available some idle rolls and these were added to the secondary crushing stage. The punched-plate trommels were replaced by vibrating screens, so that when the large-scale grinding test was started all new feed was between 1 and 2 per cent on 3 mesh. In fairness to the old system of grinding, the finer crushing raised the tonnage ground to the required fineness in the old two-stage sections about 100 tons per unit; that is, from 1050 to 1150 tons per 24 hours.

## New Grinding Plant

As would be expected, the new grinding plant did not come into being immediately on the completion of a year's operation of the test section. Although the estimated saving of between 3¢ and 3½¢ per ton on the crushing and grinding cost was decidedly enticing, particularly at a normal daily tonnage of 4800 tons, there were many important considerations to be studied.

In the first place, the location of additional 12-in. FX classifiers either above the 7 by 15-ft. mills as in the test section or alongside the mills was not particularly desirable, but either arrangement could be made. Locating the classifiers alongside naturally would facilitate the closed circuiting and reduce pumping costs, and it seemed the more reasonable even though it meant moving some craneway support columns several feet to the side.

At this time, however, it was decided to mine some ore directly beneath the grinding department of the main milling plant, which would require moving the grinding sections, therefore the design of a completely new and separate grinding plant was started in the latter part of 1936. In

October 1937 the new grinding plant (Fig. 2) was completed and fine grinding was shifted from the old mill to the new plant.

The new feed is conveyed from the crushing plant by a series of conveyors to a new fine-ore bin adjacent to the grinding plant. These conveyors are entirely covered over on account of the severe climatic conditions during eight or nine months of the year.

The fine-ore bin is of rather unusual design. It is an inverted cone of 10,000 tons capacity, of which about half the depth is below the ground level. The inner surface is smooth concrete. The dome-shaped cover has a structural-steel framework with a laminated wood covering and this, in turn, is covered with heavy weather-proofing. A motor-driven carriage with a boom attached to it and to a swivel at the top of the dome roof carries a loop of steel cable to which is attached a heavy chain drag, made more positive in its scraping action by short pieces of steel rail attached to the chain. The drag can be raised or lowered by a motor-driven pulley arrangement, so that a circle of any size within the bin can be scraped. The scraper needs to be operated only occasionally during a shift and is an entirely effective way of maintaining the load in the ore chutes at the bottom of the bin.

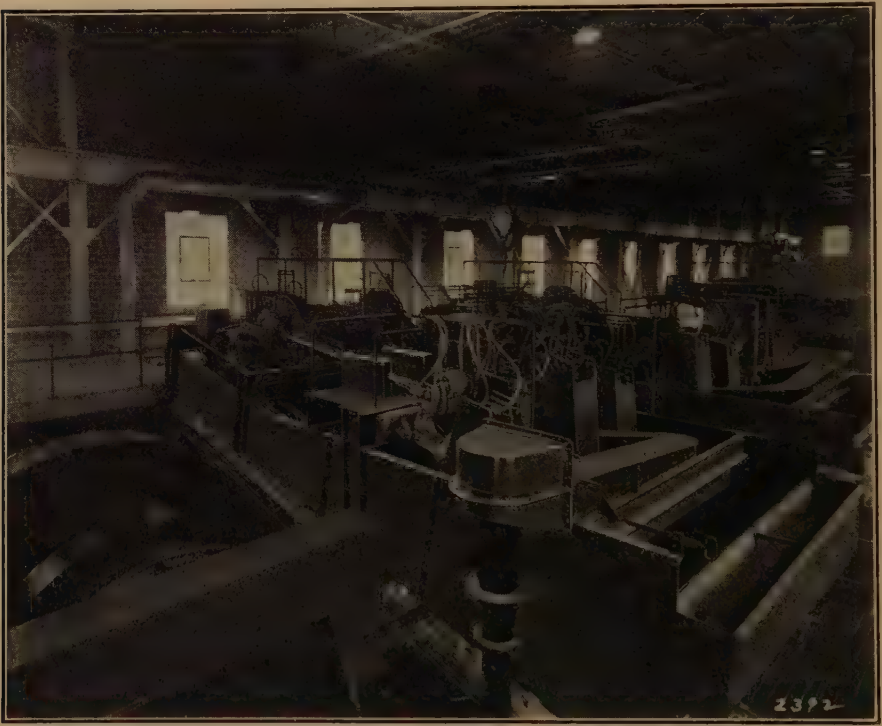


Fig. 2.—New grinding plant at Hollinger Consolidated Gold Mines Ltd.

At the bottom of the cone-shaped bin are four chutes with adjustable gates, which feed onto four short variable-speed belt conveyors, each of which feeds onto an inclined conveyor belt that carries feed to a ball mill and classifier unit in the grinding plant. The control of the variable-speed conveyors is arranged so that the amount of feed on the belt may be regulated at the operator's station. The new feed enters the mill scoop box where it is picked up with the returning rake sands by the 72-in. diameter double-acting mill-feed scoop.

There are four 7 by 15-ft. (6 ft. 6 in. by 14 ft. 6 in. inside liners) low-discharge ball mills, three of which are driven at 24.5 r.p.m. by 350-hp. motors. The fourth unit is driven by a 350-hp. two-speed motor, which normally drives the mill at approximately 12.5 r.p.m. but which can be stepped up to the 24.5 r.p.m. speed of the other mills when full tonnage is required from this unit. With each ball mill handling 1500 tons, there is only 500 to 600 tons remaining for the fourth mill to grind, and the slower speed of 12.5 r.p.m. handles the reduced tonnage comfortably. Each mill has a grate discharge the full diameter of the mill with ⅜-in. free openings. The grate end of the mill is open and the pulp discharges directly into a launder. Smooth liners are used and the ball load is maintained at or near the center line with 2½-in. balls, which, as mentioned previously, have been found adequate for the new feed, which has all passed a $\frac{3}{16}$ by ½-in. mesh screen.

In closed circuit with each of the mills is a Dorr Quadruplex FX classifier, type QSFX, 12 ft. 0 in. wide by 27 ft. long. The classifiers are set on a slope of 2¼ in. per foot and driven by 18-hp. constant-speed motors. The height of the overflow weir is 50½ in. and a cross baffle is used in the classifier pool, set at 31 in. in the horizontal direction from the weir and with a submergence of about 10 to 12 in. The most satisfactory rake speed is about 24 s.p.m. The classifier operating with the mill having the two-speed motor has a longitudinally divided tank and only 6 ft. of width is used on the reduced tonnage.

To complete the closed circuit, 6-in. sand pumps are used for pumping the mill discharge against a total head of 19 ft. up into the classifiers. These pumps are rubber lined with linotex and white-iron impellers are used. The motors are 25 hp. to drive the pumps at 510 r.p.m. Although the pumps are of the 6-in. size, 8-in. suction and 8-in. discharge lines were found most satisfactory.

A Morris centrifugal pump is used. It has 6-in. intake and discharge. Its connected horsepower is 25; consumption is 26 hp. and cost, 0.162¢. The impeller is white iron and its life is 23 days. Maintenance cost is 0.232¢ per ton of new feed to mill. Total cost, power and maintenance, is 0.394¢. This pump has capably handled all loads imposed to date, including some circulating sand tonnages well above the 4 or 5:1, which is the normal.

The various control gauges and mechanisms in the new grinding plant were very carefully thought out and are a great asset to steady operation and consistent performance in the grinding plant. Conveniently situated at the operator's station are the ball-mill ammeter, the recording weightometer and new feed control, the solution pressure gauge and all necessary gravity charts. A tank on the floor below the classifiers measures classifier rake tonnages. At each classifier overflow is a gravity scale with sample can for specific gravity determinations on the classifier overflow.

It was found during the experimental test that the low-discharge ball mill was fairly sensitive to feed-rate adjustments. Underfeeding the ball mill, with its consequent light rake load on the classifier, sends the power demand up sharply and, conversely, overfeeding with a steadily increasing rake load shows a sharp drop in the ampere demand. By means, then, of an ammeter with a reasonably large recording range, the operator can control the rate of feed to the mill to obtain and maintain the maximum grinding capacity. It has been demonstrated that at "full circulating load the power consumption is 386 hp. The reading of the ammeter needle at that time was 318 with a swing from 315 to 320. The operator knows the mill to be entering an underloaded state if his needle swing moves over 320 to 325 and continues to stay there. Again, if his needle drops to swing between 310 and 315, he is suspicious of overfeeding, and when it goes below 310 he must cut the feed rate or have a definitely overloaded condition." Little attention is paid to the fineness of the feed by the grinding-plant operators, as they rely wholly on the ammeter to regulate the feed rate.

A modern dust-collecting system about completes the well-planned features of this new grinding plant. Dust-collector covers are installed over all feed belts, on the mill-discharge grates and over the sand-return launders; which, incidentally, effect a gravity return of rake sands to the mill scoop boxes. The dust recovered by the collecting system is returned to the mill circuit.

## Operation of New Plant

The operation of the new grinding plant for the past year has been thoroughly encouraging and gratifying to those who had the vision to plan and construct it. Summarized, it has been as follows:

*Ball Mills*

| New Feed | | New Feed | | New Feed | |
|---|---|---|---|---|---|
| Mesh | Per Cent | Mesh | Per Cent | Mesh | Per Cent |
| 3 | 0.8 | 14 | 54.6 | 65 | 77.7 |
| 4 | 8.3 | 20 | 60.7 | 100 | 80.6 |
| 6 | 21.4 | 28 | 65.4 | 150 | 82.6 |
| 8 | 34.3 | 35 | 70.7 | 200 | 84.7 |
| 10 | 45.1 | 48 | 74.7 | –200 | 15.3 |

*Power.*—374 hp. with new liners to 460 hp. with well-worn liners. (Motors are actually 400 hp.)

*Steel Consumption.*—1.2 lb. per ton ore ground.

*Liner Wear.*—A set of 3½-in. manganese shell liners lasts approximately 230 days and a set of white-iron liners lasts 200 days, but the cost per day of the latter is approximately 40 per cent less than that of the former.

*Tonnage.*—Up to 1630 tons can be handled when the mill liners are worn down.

*Mill Discharge.*—Specific gravity, 2.0 or 76.5 per cent solids; 2.90 sp. gr. dry solids.

### *Classifiers*

*Circulating Load.*—Averages 4.3 to 1 on 1500 tons feed, or 6450 tons of rake sands.

*Total Load through Mill.*—6450 plus 1500 tons, or 7950 tons per 24 hours.

*Repair Costs.*—Nil during first year's operation.

*Solids in Overflow.*—33 to 35 per cent.

### *Screen Analysis*

The following screen analysis is from a composite sample taken over 24 hr. on Aug. 2, 1938, and is fairly representative of the general day-to-day operation. The analysis headed "Old Method" is the result of screening by the method employed in the Hollinger laboratory for many years. This method consisted of drying the sample, cutting out the required 500 grams for the screen analysis and then screening dry on a shaking mechanism, using glass beads on the screens. The analysis headed "New Method" is along the lines of the generally accepted standard: namely, (1) drying of sample, (2) cutting out the 300 or 500 grams for analysis, (3) washing through a 200-mesh screen, (4) drying the plus 200 mesh, (5) screening on a Ro-tap for a specified number of minutes.

| | Old Method, Per Cent | New Method, Per Cent |
|---|---|---|
| + 35 mesh | 0.1 | 0.9 |
| + 48 mesh | 3.0 | 6.4 |
| + 65 mesh | 9.8 | 17.3 |
| +100 mesh | 19.4 | 28.3 |
| +150 mesh | 28.6 | 38.3 |
| +200 mesh | 36.6 | 46.8 |
| −200 mesh | 63.4 | 53.2 |

## SUMMARY

1. Figs. 1 and 2 show the two-stage arrangement, as of 1931–1934, and the present single-stage arrangements, as of 1938. The comparative operating data appended to each flowsheet show the improvements made and the extent of the improvements.

2. The two flowsheets differ in three chief respects; i.e., the elimination, as of 1937, of the two secondary pebble mills; the changing of the former rod mills to ball mills of the low-discharge type, and the providing of additional classification capacity in the form of heavy-duty FX units.

3. Four new sections, each consisting of a 7 by 15-ft. ball mill and a 12 by 27-ft. classifier, now are capable of handling 5500 to 6000 tons of feed per day, which is about the same tonnage handled previously by the six old and more complicated sections, each consisting of a 7 by 15-ft. rod mill, two 6 by 16-ft. pebble mills and two 6 by 29-ft. classifiers.

4. On a sectional basis, a single new section handles 1335 to 1630 tons per day at a power consumption of 407 to 500 hp. compared with 950 tons and 479 hp., respectively, in an old section. The difference in power and tonnage per ball-mill unit depends on the diameter of the mill. With new liners (77-in. mill diameter) the power reading is 375 hp. and the tonnage 1335. With worn liners (82-in. mill diameter) the power reading is 460 hp. and the tonnage 1630. In both cases the ball load is kept at center line, or 50 per cent of the volume of the mill.

5. In unit power consumptions, the new plant requires 7.32 to 7.36 hp-hr. (5.46 to 5.49 kw-hr.) per ton of new feed, whereas the corresponding figure for the old plant is 12.10 hp-hr. (9.03 kw-hr.). This represents a reduction in unit power consumption of between 39.6 and 39.2 per cent.

6. Fineness of grinding is substantially the same for both methods, about 63 per cent minus 200 mesh. Feed is also substantially the same in so far as minus 200 mesh is concerned—13 to 15 per cent. The new section, however, produces more minus 200 mesh per day than the old one, 721.5 tons (1500-ton rate) as against 470 tons (950-ton rate), and likewise excels in the amount of power required to produce a ton of minus 200 mesh, 1.02 hp. as against 0.63 to 0.64 hp., a unit power reduction of 37.2 to 38.2 per cent.

7. The over-all improvement from an economic standpoint is 3.33¢ per ton ground, or $160 per day, based upon an over-all cost of both crushing and grinding from 1931 to 1934 of 21.26¢ per ton and upon the corresponding figure for 1938 of 17.93¢ per ton—daily output being taken as 4800 tons. In 1938 there was a direct increase of over 10 per cent in the over-all crushing and grinding cost above that of 1931 to 1934, owing to an increase in the hourly wage rate and price of supplies. The actual 1938 cost of 19.92¢ has, for purpose of comparison, been reduced by 10 per cent, to 17.93¢ per ton for crushing and grinding.

### ACKNOWLEDGMENT

The author wishes to acknowledge the kind assistance and the data given by Mr. E. L. Longmore and Mr. Maurice E. Williams, General Superintendent and Mill Superintendent, respectively, of the Hollinger Consolidated Gold Mines Ltd., and again mention the happy spirit of cooperation engendered into the work by the whole Hollinger milling staff during the time when the author and several other members of his firm were present helping to carry on the large-scale testing operation.

## DISCUSSION

O. H. JOHNSON,* Denver, Colo. (written discussion).—Mr. Hitzrot's paper is interesting because it describes how simply and efficiently the staff of the Hollinger Consolidated Gold Mines Ltd. reconstructed and rearranged the milling plant and made good use of much of the previous equipment.

During the year 1921, the Hollinger company was considering replacing its stamps with ball mills, with the idea of increasing the capacity of the milling plant to 8000 tons. In the fall of that year, I called upon the management and staff and discussed and recommended that they give consideration to the use of rod mills ahead of their tube-mill grinding; and in November 1921 The Mine and Smelter Supply Co. arranged with the Hollinger company, on a trial basis, for the installation of a 5 by 10-ft. Marcy open-end rod mill. This mill was shipped April 4, 1922, and was under test during that year. The results were so satisfactory that the Hollinger company paid for this test mill and ordered eight rod mills, which were the largest that had been built up to that time. These eight Marcy rod mills measured 7 ft. in diameter by 15 ft. long inside the shell. Five of these mills were shipped in July 1923 and three more were shipped Aug. 31, 1926.

These are the mills that were moved, re-erected and converted into the open-end ball mills described by Mr. Hitzrot. These mills were easily converted because they are mounted on tires and rollers and all that was necessary was to replace the big open-end rod-discharge heads with the low-discharge grates.

Previous records, notes and publications disclose that a section of a rod mill and two tube mills always averaged a classifier overflow product of 66 per cent minus 200 mesh. The feed to these rod mills during their earlier operation was much coarser than in the later years.

---

* Vice President, Mine and Smelter Supply Co.; Manager, Marcy Mill Division.

# Closed-circuit Grinding of Cement Raw Materials at Leeds

By T. B. Counselman,* Member A.I.M.E.

(New York Meeting, February, 1939)

After several years study, the Universal Atlas Cement Co. decided to rebuild its plant at Leeds, Alabama. The entire old plant, which was to operate during the new construction, was then to be scrapped with the exception of two kilns. The quarry was to be mechanized, new and larger kilns installed, with the most modern type of equipment all through the plant.

Raw grinding operations at all of the Universal Atlas plants were dry. However, the dust hazard of this operation and the growing emphasis on occupational diseases made wet grinding attractive. Coal at Leeds is cheap, so that a slightly higher coal practice was unimportant. Power was cheap, so that waste-heat boilers were not desirable. Since new kilns were to be installed, these could be made long enough to make filters unnecessary.

Wet raw grinding could be either the old practice of open-circuit compartment mills or closed-circuit grinding in accordance with metallurgical practice. The latter saved power and steel wear and saved initial investment. This had been demonstrated in cement plants. Also, the elimination of tramp oversize was a most important advantage. Ease of chemical control was another factor. Blending in the thickener, with elimination of slurry mixers had been found practicable. Therefore, if wet raw grinding were used at all, the advantages were clearly in favor of closed-circuit grinding. Detailed layouts of the most modern possible closed-circuit dry-grinding plant and of a closed-circuit wet-grinding plant were prepared, and careful estimates were made of initial investment and operating costs. Full consideration of all the factors involved resulted in a decision to install wet closed-circuit grinding.

The capacity of the new kilns was established at 4000 bbl. per day. Two new kilns were installed, each with a capacity of 80 bbl. per hour. Since 625 lb. of raw material is required to make a barrel of finished cement, the capacity of the grinding plant for the new kilns had to average only 1250 tons per day. Sufficient additional grinding capacity had to be provided for the two remaining old kilns, or their possible replacement by a third new kiln. The grinding rate, therefore, was set at 90 tons per

---

Manuscript received at the office of the Institute Dec. 10, 1938. Issued as T.P. 1096 in Mining Technology, July, 1939.

* Manager, Industrial Division, The Dorr Company, Inc., Chicago, Ill.

hour, which would permit the equivalent of two shifts per day, or actually 14 hr., to grind the tonnage required for a 4000-bbl. production, with sufficient remaining time to grind the requirements for the two old kilns. This grinding equipment was planned to be divided into two parallel units, for flexibility.

Cement plants are becoming more and more chemical plants, and must be able to produce several different kinds of cement, as called for by orders. These different cements require varying proportions of raw materials; at Leeds, for example, limestone, shale and sandstone, with sometimes the addition of a fourth raw material, iron ore. The storage capacity of raw ground slurry in a thickener is roughly sufficient for a week to ten days of burning. Therefore, to provide flexibility and permit switching at will from one kind of cement to another without loss of burning time, it is desirable to have two thickeners.

Then, if the plant were producing standard cement, with a thickener full of raw slurry, and a run on some special cement were desired, grinding of the new mix into the empty thickener could be started while the burning of slurry from the full thickener could be continued for a few days until ready to cut the kilns over to the special mix. Therefore, each of the thickeners should be large enough to handle the maximum grinding rate of the raw grinding department.

A certain amount of storage of finished, thick slurry ready for burning should be available at the kilns. Therefore two slurry mixers were required under each kiln, as kiln-feed tanks, each capable of storing a supply of slurry for about 8 hr., one tank to be filling while burning was done from the other. It is notable that no correction tanks and no additional storage of thick slurry is necessary. The thickener takes the place of both correction tanks and large slurry-storage basins.

The Leeds plant is somewhat unusual in that the raw materials come from separate quarries, are handled separately into the plant, and can be accurately proportioned from the start. This, of course, greatly facilitates chemical control, and helps to account for the excellent cement that has always been produced at Leeds. The shale is sticky when wet, and in the limestone quarry there are occasional seams of sticky clay. In hand quarrying, these clay seams were rejected, but it was recognized that in mechanized quarrying they could not be avoided. This limited crushing ahead of the ball mills to one-inch maximum size. Any attempt at finer crushing would give trouble in the crushers and hammer mills. Therefore large samples of each of the various ingredients were crushed to one-inch size, and sent to the Westport mill of The Dorr Company, Inc. at Westport, Connecticut. Careful tests were made on the proper proportions of these raw materials to determine grindability, classification characteristics, and thickener requirements, and in accordance with these tests the flowsheet shown in Fig. 1 was drawn up.

## Quarrying and Crushing

In the limestone quarry, standard quarry methods of stripping by scrapers and drags, churn drilling and big-hole blasting are used. A 2½-yd. electric shovel loads the stone into 12-yd. cars of a Woodford haulage system, the control tower for which is at the crusher building. The cars are dumped from the control tower, by an electric dumper, into a 42-in. gyratory crusher. There is a small storage hopper below this, from which the stone is fed by a pan conveyor to a 42 by 66-in. hammer mill, which is set to crush to one inch. No screens are used. A dust-collecting system operates on the housed-in hammer mill and pan conveyor, delivering to the belt conveyor, which takes the hammer-mill product a few feet to the stone storage. There a 100-ft., 10-ton traveling crane, with 3-yd. bucket, distributes the material to the proper point in the rock-storage yard.

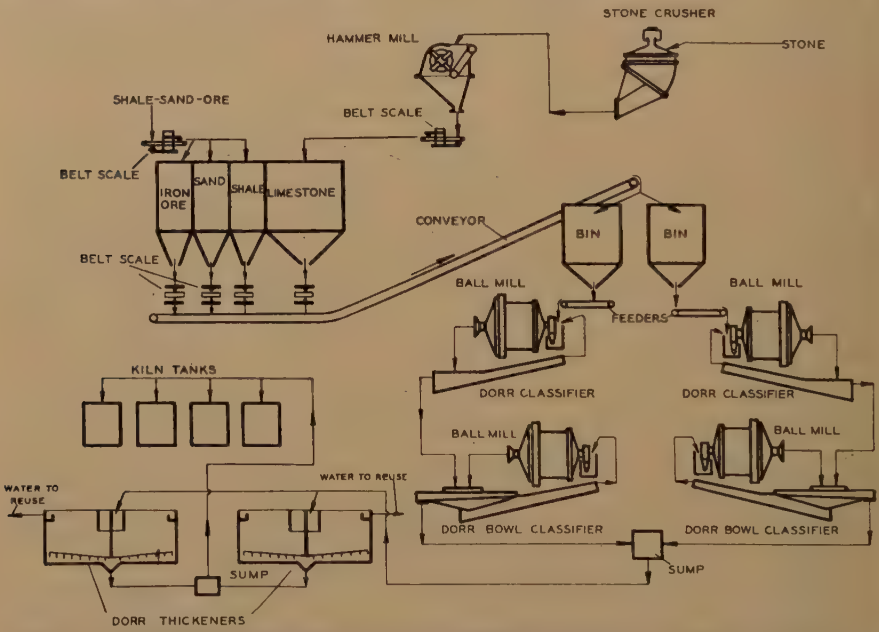


Fig. 1.—Flowsheet, Universal Atlas Cement Company at Leeds, Alabama.

The shale and sandstone are quarried separately; sandstone by hand methods, shale with a small electric shovel. A No. 5 gyratory and a hammer mill crush the product of either quarry to a nominal one-inch size. The crushed materials are hauled to the plant, by railroad or trucks, and dumped onto a conveyor, which delivers to the rock storage. The bridge crane stores the two materials in separate piles, at the opposite end of the yard from the limestone. At one side of the yard, the bridge crane dumps the different materials into four different hoppers, below each of which is a belt scale. These hoppers can be set to give any desired proportion of various raw materials, delivering to a conveyor, which carries the mixture to the raw-grinding building.

### *Raw Mill*

There is a 25-ton surge bin ahead of each grinding unit, and the entire stream of raw material is diverted from one to the other, automatically, at 5-min. intervals. A bin indicator tells the operator the condition of each bin, and by cutting out the automatic device, he can fill either bin as desired, or stop the feed entirely.

Constant-weight feeders withdraw material from these surge bins to the primary ball mills, thus keeping them up to maximum grinding capacity. This was found to be very important.

Two-stage grinding was necessary to reduce 1-in. material to 200-mesh. In selecting the ball mills, it was felt desirable to have the primary and secondary mills of exactly the same size, so that all parts would be interchangeable. After study of the grindability tests, mills were specified to be 9-ft. diameter inside the liners by 8 ft. long from the head liner to the grid plate. Throat and discharge trunnions are 22 in. and 24 in. clear diameter. The feed scoops are 4-ft. 0-in. radius. The discharge grates of the primary mills have slots ⅞ in. wide inside, tapering to 1 in. outside, and the plates are 1½ in. thick. On the secondary mills the tapered slots are ⅜ in. wide inside by ½ in. wide outside, same plate thickness. These slots extend inward for 13 in. from the inside of the liners toward the axis of the mill, the central portion being blanked off. All of the material passing through the mill must therefore pass through these slots near the periphery, so that these are low-level mills. Internal radial lifters inside the discharge head raise the mill product to the discharge trunnion, and are so arranged that there is no spillback through the slots. The mills have water-cooled, babbitted bearings.

The primary mills rotate at 19 r.p.m. and are fed heat-treated steel balls 4 in. in diameter, of about 500 Brinell. The secondary mills run at 17 r.p.m. and 2-in. balls are fed as make-up. Mixed charges were put in the mills at the start. Motors are 350 hp., 180-r.p.m. synchronous, 2200-volt, capable of 100 per cent overload at 40° C. temperature rise.

The discharges from the primary mills flow by gravity at a slope of 1³⁄₁₆ in. per foot to 8-ft. by 25-ft. 6-in. heavy-duty Dorr Multizone classifiers with 20-hp. motors. These machines will dig themselves out even when shut down under full load. Actual power consumption is about 12 hp. Sands are conveyed to the primary ball-mill scoop boxes by vibrating launders having 7½-hp. motors.

Fig. 2 shows the arrangement of the primary and secondary grinding circuits, with the Multizone classifier in the primary circuit and the bowl classifier in the secondary.

The overflows of the Multizone classifiers go by gravity, in a launder having a slope of 2 in. per foot, to the heavy-duty Dorr bowl classifiers, which are 16 ft. wide by 39 ft. long by 24 ft. in diameter, and any finished material overflows without getting into the secondary ball mills. The rakes of these machines are driven by 20-hp., constant-speed motors, actually taking 13 hp. with normal load. In most cases of a sudden shutdown under load, the rakes have been able to dig themselves out without draining the machine. The bowl is driven by a 10-hp. motor with a variable-speed reducer to provide adjustment for helping control the fineness. Actual power consumption is about 6½ horsepower.

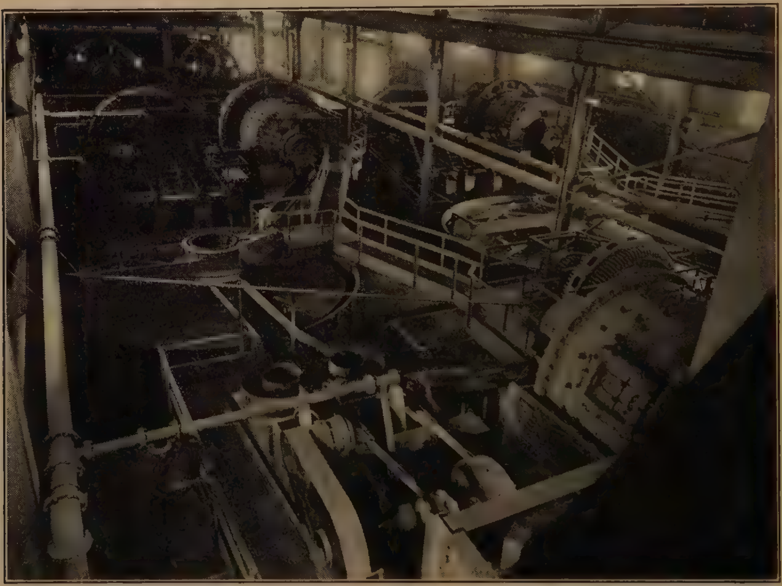


FIG. 2.—RAW-GRINDING DEPARTMENT, UNIVERSAL ATLAS CEMENT COMPANY.

The rake products of these classifiers are elevated by 12-ft. diameter sand wheels, rotating at 9½ r.p.m., driven by 10-hp. motors, and flow down a slope of 4½ in. per foot to the scoop boxes of the secondary ball mills described above. The ball-mill discharges flow to the bowl classifiers, the launder slopes being 1⅝ in. per foot.

The overflows of the two bowl classifiers flow by gravity to a sump, and from there are pumped by one of two rubber-lined pumps, with 75-hp. motors at 2500 gal. per min., through a 12-in. line to the distribution box between the two Torq thickeners.

## THICKENERS

These thickeners, 200-ft. diameter by 10-ft. side-wall depth and 20-ft. center depth, have a bottom slope of 2 in. per foot for a diameter of 80 ft., and a slope of 1 in. per foot from there to the periphery. There are two long arms of Torq construction, which raise automatically in case of an overload. They have no blades within the 80-ft. diameter of the steeper bottom. There are also two short arms with blades to rake material within this 80-ft. diameter. These arms are hinged somewhat like Torq arms, but are locked into position so that they do not raise automatically, although they can be readily raised in case of necessity.

On the long arms are mounted rubber-lined recirculation pumps with 10-hp. motors, which run at 100 gal. per min. and pick up slurry at any desired level, varying from the discharge cone at the bottom, where the slurry is thickest, up to the surface at the feed well, and pump it out two-thirds or more of the distance to the periphery. The discharge lines are so arranged that the slurry can be discharged at the bottom of the thickener or at any desired elevation. The objective, of course, is to discharge slurry, of whatever consistency, drawn into the recirculating pump, into a zone of practically the same consistency. In this way, thick slurry is not redispersed and does not have to be rethickened. Due account must be taken of the dilution of the slurry by the gland water of the pumps, otherwise the water content of the thickener underflow will be increased.

Gland water for the recirculating pumps is obtained by auxiliary 1-in. water pumps. The suction lines of these pumps run out each long arm and terminate, through a rubber hose, in a fitting fastened to a float. Thus clear water from close to the overflow rim is obtained for gland water.

The capacity of the recirculating pumps is equal to the average withdrawal requirement from the thickener. The purpose of this recirculation is to give thorough blending, as to chemical composition and particle size, of the solids in the thickener. Without such recirculation the coarser particles (which are also usually higher in lime and silica, and lower in alumina, than the average composition) tend to settle quickly to the bottom near the center. When not grinding in the raw mill, this coarser fraction is withdrawn first, and subsequent withdrawals consist of much finer material. This carries more water, because of its fineness, and also carries lower lime and higher alumina. It is the increased amount of water in this finer slurry that is serious. Recirculation tends to minimize these variations.

These thickeners rotate at one revolution in 40 min. They are carried so full of slurry that the line of the top of the slurry is at times only a foot or so below the water level. Records show that each thickener then contains about 32,000 bbl. of slurry, or, roughly, a week's supply for both kilns. In spite of over 10,000 tons of solids in each of these machines, the heliocentric drive is so perfectly balanced that the ammeter reading shows about 2-hp. consumption. The drive units are 5-hp. vertical motors, direct-connected to speed reducers, driving through a double train of spur gears, an internal ring gear to which the thickener mechanism is fastened. This large ring gear rests on a continuous circle of 1¼-in. steel balls, running in oil, and forming in effect a very large ball bearing, mounted on the center pier. The mounting is such that the motor floats and delivers power equally to each train of gears.

In case of an overload, such as starting up after a power interruption, the long Torq arms would rise slightly and equalize the load on the motor. If the motor could not then pull out, the short arms could be raised manually by a lifting device provided for the purpose, the arms being hinged in a somewhat similar manner to the Torq arms. There is an overload device on each machine which, at a 20 per cent overload on the motor, or if the mechanism stops rotating, sounds a horn. If the load is not relieved (by starting the underflow pumps and recirculating back to the thickener, for example) and the overload on the motor increases to 30 per cent, the motor will then kick out. The alarm horn must be reset before the motor can be started.

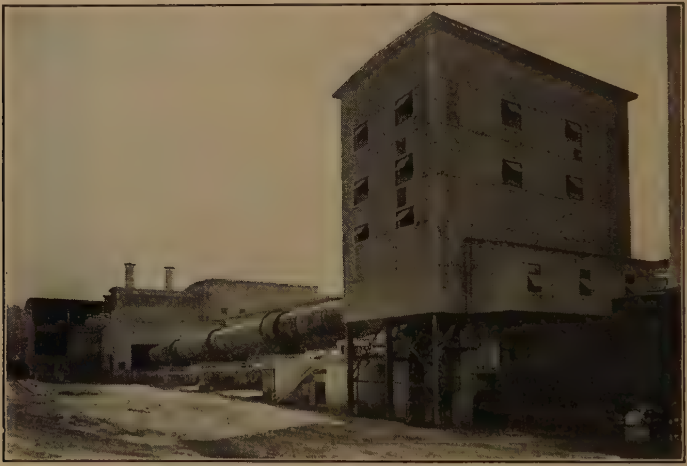


FIG. 3.—KILN WITH SLURRY MIXERS.

The slurry is withdrawn by gravity, through any of four 6-in. lines from the discharge cone, and thence through an 8-in. underflow line to a feed sump for the slurry pumps. Flow through the underflow lines is controlled by orifice plates in the line, and also an electrically operated valve shuts off the flow from the thickener in case of a power interruption. There are two of these slurry pumps, 4 in. in size, each driven by a 75-hp. motor, one pump being a spare. Piping is arranged so that they can deliver to the kiln-feed tanks through an 8-in. line, or recirculate to the feed-distribution box between the thickeners.

Fig. 3 shows one of the kilns, with the kiln-feed tanks. There are four Dorr slurry mixers, serving as kiln-feed tanks, two under each kiln, near the feed end. These are 24-ft. dia. by 16 ft. deep, driven by 7½-hp.

motors at 17 r.p.m., and carry sufficient slurry for 8-hr. operation of one kiln. By this arrangement, and because there are two thickeners, with only some minor piping additions from the slurry mixers to the feeders, it would be perfectly possible to burn a different type of cement in each kiln simultaneously, if desired.

Slurry from these kiln-feed tanks is pumped by slurry pumps to constant-volume kiln feeders, at about twice the burning rate, a uniform amount being fed by gravity to each of the 10-ft. dia. by 300-ft. long kilns, the excess slurry being returned to the kiln-feed tank.

## Water System

Thickener overflow is pumped by either of two 3000-gal. per min. pumps, equipped with 75-hp. motors, through a 10-in. line to a constant-level tank 10 ft. in diameter by 11 ft. deep, located 25 ft. above the main water lines in the raw mill. This tank has an emergency overflow to the sewer, and also a make-up new water line, controlled by a float valve, to keep the tank always full. There is a separate 10-in. main water header, controlled by a single master valve, for each grinding unit, this valve being closed when the unit is shut down. In this way the spray valves throughout the units are always left in approximate adjustment.

The amount of new water available would be entirely inadequate alone to operate the raw mill without return from the thickeners. In starting up, there is 5000 gal. available in the constant-level tank. The system is usually left full, so that as soon as the master valves are opened and the bowl-classifier overflow pumps are started water reaches the thickener, overflows, and is returned by the 3000-gal. per min. centrifugal water pumps to the constant-level tank. Actually the make-up water need only be sufficient to compensate for the water in the slurry, which is evaporated in the kilns, for solar evaporation from the thickeners and any accidental spills to the sewer.

## Operating Results

Plant operation was started in June 1938 and tuned up gradually. The raw-grinding department started off smoothly, only minor adjustments being required, and within a few days was operating steadily at about 85 per cent of rated capacity. At the time this is written (November 1938) the feed rate is set at about 110 tons per hour, or 122 per cent of rated capacity, and the unit runs out of feed occasionally, this tonnage being the present top capacity limit of the Feedoweights. Typical results when grinding at approximately this capacity are given in Table 1.

## Power Requirements

In addition to more uniform grinding, one of the principal advantages of closed-circuit grinding is saving in power. At one plant having open-circuit wet grinding in a two-compartment mill, the power required for the mills alone for raw-grinding enough material to make a barrel of cement (the relative grindability of the mix being almost the same as at Leeds), amounted to about 7.5 kw-hr. At Leeds, when grinding in one unit 54 tons per hour, equivalent to 173 bbl., the power readings were as shown in Table 2.

The total raw grinding requires approximately 4¼ kw-hr. per barrel, at the above output rate, but this includes various conveyors, pumps and handling equipment, which would be required in any event. The recirculation pumps in the thickener are not included, because these are part of the blending system, and really a considerable saving in power over the usual correction tanks and slurry basins.

TABLE 1.—*Typical Results, November* 19, 1938

| Opening | New Feed | Primary Mill Discharge | Primary Classifier Sands | Primary Classifier Overflow | Secondary Mill Discharge | Bowl Classifier Sands | Bowl Classifier Overflow | Primary Circulating Load | Secondary Circulating Load |
|---|---|---|---|---|---|---|---|---|---|
| UNIT NO. 1.[a] ⅞-IN. WIDE SLOTS IN PRIMARY MILL GRATES | | | | | | | | | |
| Inch | | | | | | | | | |
| +1 | 2.6 | | | | | | | | |
| +¾ | 5.4 | 0.3 | 1.2 | | | | | | |
| +½ | 10.7 | 3.7 | 3.5 | | | | | | |
| +⅜ | 23.0 | 6.8 | 7.1 | | | | | | |
| Mesh | | | | | | | | | |
| + 4 | 45.7 | 13.2 | 16.1 | | | | | | |
| + 5 | 48.3 | 14.5 | 18.2 | | | | | | |
| + 8 | 62.5 | 21.9 | 32.1 | | | | | 214 | |
| + 14 | 74.0 | 37.2 | 58.7 | 1.6 | | 0.4 | | 166 | |
| + 28 | 84.5 | 61.2 | 86.5 | 18.6 | 2.1 | 7.4 | | 168 | 351 |
| + 48 | 89.0 | 75.0 | 94.0 | 37.4 | 15.1 | 26.1 | | 198 | 340 |
| +100 | 92.2 | 81.6 | 96.2 | 52.1 | 48.8 | 64.0 | | 202 | 342 |
| +200 | 94.0 | 85.4 | 97.0 | 61.0 | 78.9 | 92.6 | 13.0 | 210 | 351 |
| +325 | | | | | | | 22.4 | | |
| Specific surface | | | | | | | 3792 | | |
| Tons per hour | 54 | 164 | 110 | 54 | 187 | 187 | 54 | Best Avg. 203 | Best Avg. 346 |
| $H_2O$, per cent | 2.3 | 23.8 | 24.5 | 50.1 | 35.6 | 23.4 | 83.9 | | |
| UNIT NO. 2. ⅜-IN. WIDE SLOTS IN PRIMARY MILL GRATES | | | | | | | | | |
| Inch | | | | | | | | | |
| +1 | 2.6 | | | | | | | | |
| +¾ | 5.4 | | | | | | | | |
| +½ | 10.7 | | 0.2 | | | | | | |
| +⅜ | 23.0 | 0.6 | 0.9 | | | | | | |
| Mesh | | | | | | | | | |
| + 4 | 45.7 | 3.5 | 7.8 | | | | | | |
| + 5 | 48.3 | 4.0 | 8.9 | | | | | | |
| + 8 | 62.5 | 9.2 | 18.9 | | | | | 95 | |
| + 14 | 74.0 | 20.6 | 41.4 | 0.6 | | | | 96 | |
| + 28 | 84.5 | 45.0 | 76.3 | 13.6 | 1.0 | 4.9 | | 100 | |
| + 48 | 89.0 | 60.5 | 89.1 | 32.6 | 8.0 | 22.6 | | 98 | 223 |
| +100 | 92.2 | 71.3 | 93.3 | 48.4 | 37.4 | 62.1 | | 104 | 196 |
| +200 | 94.0 | 76.6 | 95.2 | 58.9 | 69.2 | 91.5 | 10.1 | 95 | 210 |
| +325 | | | | | | | 19.2 | | |
| Specific surface | | | | | | | 4093 | | |
| Tons per hour | 50 | 100 | 50 | 50 | 102 | 102 | 50 | Best Avg. 100 | Best Avg. 203 |
| $H_2O$, per cent | 2.3 | 32.8 | 21.6 | 55.2 | 34.2 | 30.5 | 84.5 | | |

[a] Approximately 6000 lb. less ball load than No. 2 unit.

### TABLE 1.—(*Continued*)

SEDIMENTATION ANALYSES OF BOWL OVERFLOWS BY WAGNER TURBIDIMETER METHOD
Assuming Average Diameter 7.5-micron Particles to be 2.6 Microns

| Particle Size | Unit No. 1 | Unit No. 2 |
|---|---|---|
| Mesh | | |
| +200 | 13.0 | 10.1 |
| +325 | 22.4 | 19.2 |
| Microns | | |
| −60 +55 | 23.4 | 20.1 |
| +50 | 25.5 | 22.6 |
| +45 | 28.8 | 25.6 |
| +40 | 31.2 | 28.3 |
| +35 | 33.2 | 31.2 |
| +30 | 37.3 | 33.2 |
| +25 | 40.9 | 37.4 |
| +20 | 44.8 | 40.7 |
| +15 | 49.6 | 45.7 |
| +10 | 56.6 | 52.4 |
| + 7.5 | 61.5 | 58.0 |

| | Test Data, Tons per Hr. | Power Readings, Kw. | | |
|---|---|---|---|---|
| Belt scale settings: Limestone | 91.0 | Primary ball mills | 290 | 310 |
| Shale | 15.0 | Secondary ball mills | 305 | 305 |
| Sandstone | 2.2 | Primary classifiers | 9 | 9.5 |
| | | Bowl-classifier rakes | 10 | 9.5 |
| | | Bowl-classifier bowls | 3.8 | 3.8 |
| | | Thickener, rotation | 1.5 for both units | |
| | | Kw-hr. per barrel | 3.58 | 4.0 |

The classifiers and thickeners are included because they are properly a part of the closed-circuit grinding system. This method of grinding, therefore, shows a direct power saving of 3.92 kw-hr. per barrel of cement, or, on a 4000-bbl. basis, a saving of 15,700 kw-hr. per day.

The power consumption of 3.58 kw-hr. per barrel, for reduction from 1 in. to 200 mesh, is equivalent to 11.45 kw-hr. per ton. This can be broken down to a consumption of 5.55 kw-hr. per ton, for reduction from 1 in. to 14 mesh, and 5.90 kw-hr. per ton for reduction from 14 to 200 mesh. This compares very favorably with metallurgical practice.

### TABLE 2.—*Power per Barrel*

| Equipment | Kw. | Kw-hr. per Bbl. |
|---|---|---|
| Primary mill | 290 | 3.44 |
| Secondary mill | 305 | |
| Primary classifier | 9 | 0.14 |
| Bowl classifier: rakes | 10 | |
| Bowl | 3.8 | |
| Thickener | 1.5 | |
| Total power | | 3.58 |

## STEEL WEAR

Ball consumption has not yet been determined with sufficient accuracy to be of value.

## CHEMICAL CONTROL

The striking feature of the Leeds plant, to the cement manufacturer, is the complete absence of correction tanks or large slurry-storage basins. Close chemical control on the basis of $CaCO_3$ content or "holding point" is carried out right from the start of grinding. The bowl-classifier overflow is sampled automatically at the thickener, at 4-min. intervals, and the accumulated sample is analyzed every 2 hr. The variation from the holding point is determined, and the belt scales adjusted accordingly. These individual samples of bowl-classifier overflow show considerable chemical variation, but if the samples for a 24-hr. or 48-hr. period average at or near the holding point, the recirculation in the thickener will blend the material so that each kiln tank will be within the permissible limit of 0.5 per cent variation from the holding point.

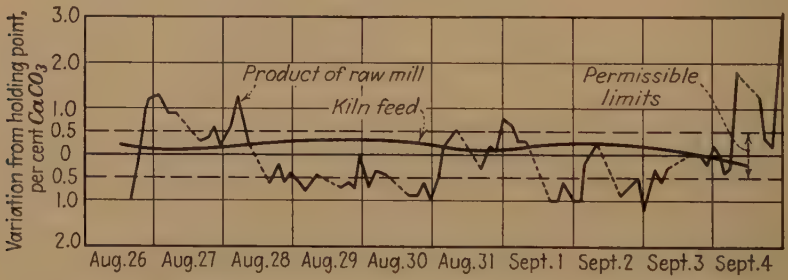


FIG. 4.—CHEMICAL BLENDING BY RECIRCULATION IN THICKENER.

Fig. 4 shows, for a typical period, the variation from the holding point of the feed to the thickener, and of the slurry withdrawn from the thickener during the same period. The smoothing out effect of the recirculation is obvious.

The importance of recirculation in the thickener, in order to get uniform chemical blending, cannot be minimized. Obviously, if there is no recirculation, the coarser particles, which are the high-lime and the high-silica particles, tend to settle out near the center, while the shale particles, carrying the alumina, grind readily to the fine micron sizes, and tend to distribute farther out in the thickener. If grinding were continuous, a uniform mixture in the thickener underflow would necessarily be obtained. On a five-day-week grinding schedule, during nongrinding periods, if there is no recirculation, withdrawal at first tends to be high in lime and silica, coarse in particle size, and low in moisture. It is highly desirable to keep the slurry as uniform as possible. Blending by recirculation in the thickener has been found entirely practical from the chemical standpoint.

Fig. 5 which is a diagrammatic cross section of the thickener, shows the principle of this blending. Essentially, thickened or partially thickened slurry is withdrawn from the center of the thickener and pumped outwardly for some distance. Such recirculated slurry should be delivered in a zone of about the same water content as the zone from which it is withdrawn, to avoid imposing extra duty on the thickener.

## Control of Slurry Moisture

Since there are no filters or other slurry-dewatering devices in the flowsheet, control of the slurry moisture assumes more than ordinary importance. The 10 by 300-ft. kilns at Leeds have a nominal capacity of 2000 bbl. per day, and this capacity has been attained.

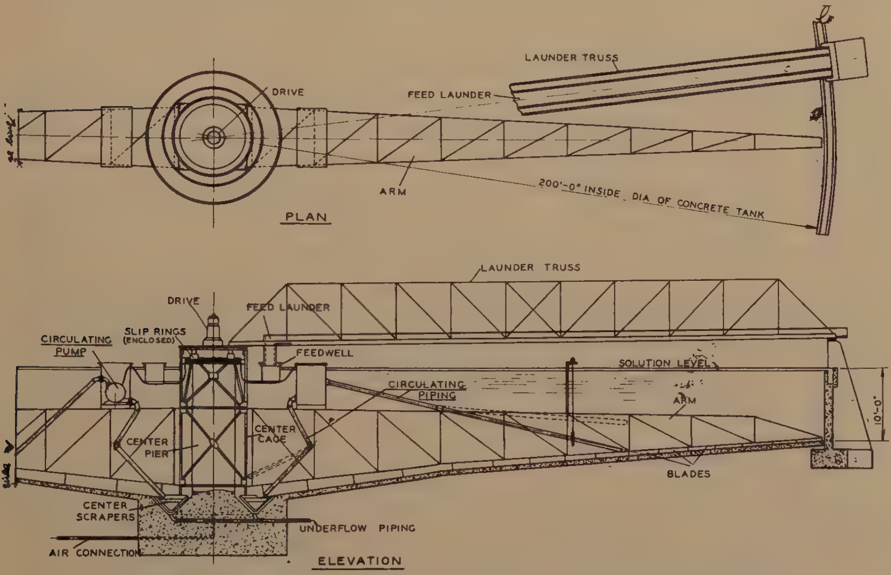


Fig. 5.—Slurry recirculation system in Dorr Torq thickener.

The kilns at Leeds are each equipped with unit coal pulverizers, so that with these and the draft available a definite maximum number of British thermal units can be introduced into the kilns. Therefore it becomes important not only to keep the slurry moisture uniform but also to keep it as low as possible. An almost constant number of B.t.u. is required to burn one cubic foot of slurry, about the same amount of heat being necessary to evaporate water as to drive off carbon dioxide, and the higher the solids content of a cubic foot of raw slurry, the higher will be the clinker output of the kiln. The kiln should properly be the bottleneck of the entire operation.

As stated above, the moisture content inevitably increases with extremely fine slurry. Therefore in the raw-grinding operation a twofold objective becomes requisite. First, everything must be ground to a limiting particle size, which permits chemical combination in the kiln. In other words, tramp oversize must be eliminated. This is thoroughly accomplished by closed-circuit grinding. Second, overgrinding and the production of ultra fines must be avoided, since these tend to hold moisture. This overgrinding may be measured by "specific surface," or square centimeters of surface per gram of dry solids, as determined by the Wagner Turbidimeter, which registers the interference to transmitted light of a dilute suspension of fine particles under standard conditions. This is the measurement that is applied to finished cement, but so far as known it has never before been applied to the closed-circuit grinding of raw materials.

The sizing analysis of Leeds slurry is given in Table 1. The specific surface of the slurry from unit No. 2 in that table is 4100, and the moisture is 35.5 per cent. It is apparent that specific surface is a very convenient single figure for expressing the relative fineness of a sample of ground material. It may apply in many instances other than in the cement industry.

As mentioned, in order to reduce the specific surface, overgrinding in the mills must be minimized. The specific surface of the slurry varied from about 3750 to 4400. This seemed high, compared with the 1600 to 2900 surface to which the clinker is usually ground, but there was no comparative experience available on other raw slurries. It is well known that in order to minimize the production of fines in a mill the circulating load must be high, and also that the pulp in the mill must be as thick as possible.

Originally table feeders were used to feed the mills, but these gave a widely varying rate, and since the setting of the water valves was practically constant there was a consequent variation in the dilution in the primary mill. To overcome this variation, constant-weight feeders were installed.

The reason for desiring a high primary circulating load is that the ultra fines are produced largely from the shale. This material goes most easily to a slime, the limestone and sandstone both being harder. After passing through the mill into the primary classifier the slime overflows, goes to the bowl classifier, where it again promptly overflows, never getting into the secondary grinding circuit. Most of the grinding (and overgrinding) of the shale, therefore, is carried out in the primary mill. If the circulating load is low, the holding time in the mill is increased, and a higher specific surface results. If the circulating load is increased, because of shortening the holding time in the mill, overgrinding is minimized.

The various steps taken so far have reduced the specific surface to about 3750, while holding the percentage of minus 200-mesh constant. With the additional steps contemplated, it is expected that a still further reduction will be accomplished. As a check against specific surface figures at Leeds, raw slurry from another plant was found to have a specific surface of 4650.

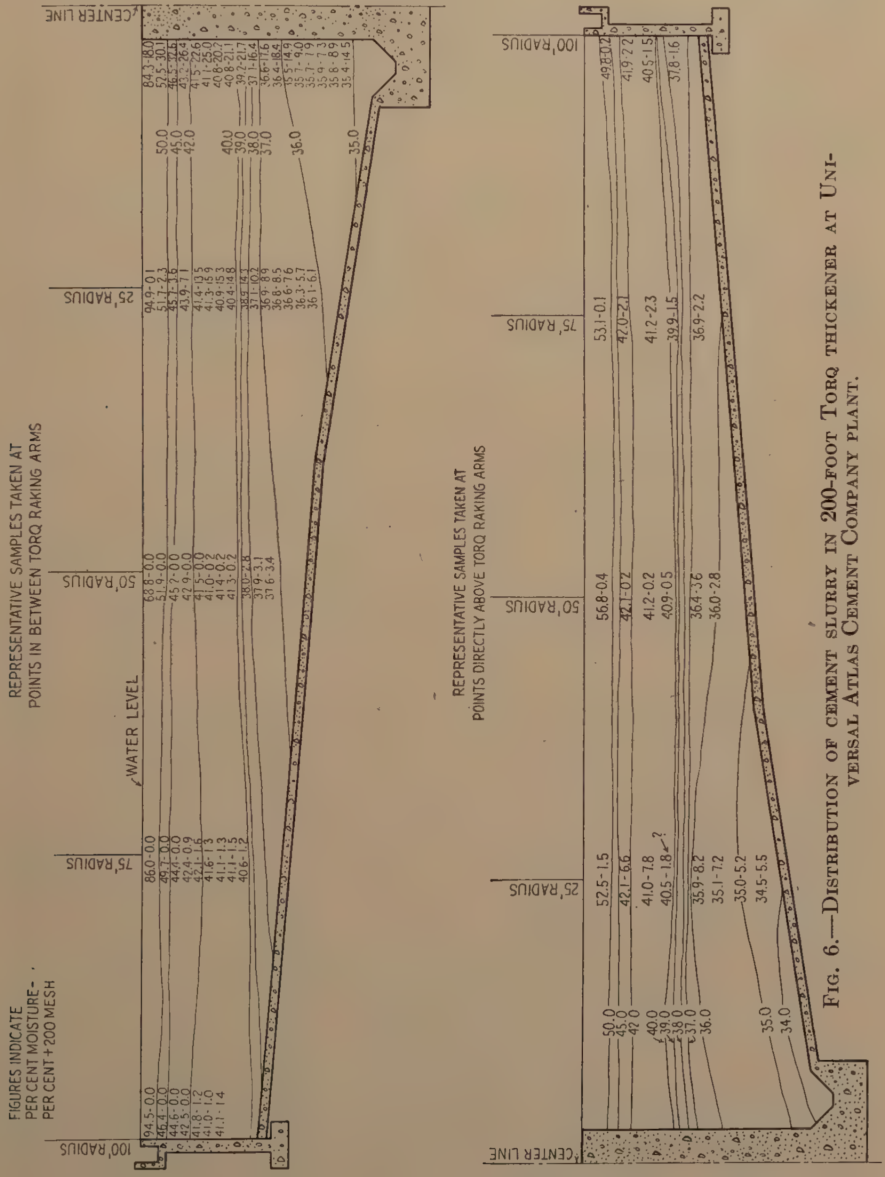


FIG. 6.—DISTRIBUTION OF CEMENT SLURRY IN 200-FOOT TORQ THICKENER AT UNIVERSAL ATLAS CEMENT COMPANY PLANT.

Having taken steps to secure the lowest possible specific surface in the grinding department, the next step was to prevent size segregation in the thickener. First of all, a very careful survey of the thickener was made. Samples were taken at every foot of depth, halfway between the rake arms, and every 2 ft. of depth directly at the rake arms, at the center and every 25 ft. outward to the periphery. The extremely interesting results of this survey are shown in Fig. 6. Samples were tested for moisture, and for residue plus 200.

The first point that is immediately apparent is that 2 ft. below the surface of the water the slurry is already 50 per cent solids. Thickening is very rapid at first, then proceeds much more slowly toward final density.

Another striking thing is the segregation of coarse particles rather high up in the thickener, at the center and for 25 ft. out from the center. As is to be expected, not much plus 200 material gets out more than halfway to the periphery. The recirculating pumps were not in operation at the time this survey was made.

As originally installed, the recirculating pump suction was down in the discharge cone. The discharge lines delivered the slurry, 33 and 67 ft. out from the center, just in front of the blades, the lines running out on each of the long arms. While the blending afforded by the recirculating pumps was excellent from a chemical point of view, it tended to increase and make cyclically variable the moisture in the slurry.

From the thickener survey shown in Fig. 6, it is obvious that the pump suction should not be in the discharge cone, but in the zone of high residue, higher up at the center. Consequently the suction lines have been hinged and made adjustable, so that the intakes can be placed at any desired elevation. At the same time the discharge lines have been made adjustable. Before this was done, an attempt was made to discharge material from about halfway up in the thickener, at the center, into the thick zone at the bottom, two-thirds of the way out. As was to be expected, this was not successful, resulting in a high-moisture slurry.

It has, of course, been found desirable to withdraw slurry from the thickener at a fairly uniform rate, and the pumping schedule has been so arranged. If no slurry is required at the kiln-feed tanks at that time, the slurry may be returned to the feed launder.

With gradually improved operation, the slurry moisture has been reduced to about 35 per cent. Pending some changes in speed, and other changes to lower this moisture still further, the second thickener, which normally is idle except when special cements are required, has been used both for storage and for a slight additional moisture reduction. The underflow from this second thickener, which constitutes the kiln feed, has been consistently lower than 32 per cent, or about a 3 per cent reduction of moisture in the second thickener. No recirculation is practiced in this unit. It is hoped, however, that when the several changes in operating adjustments now being carried out in the first thickener have been completed, this low moisture will prove readily obtainable in the underflow of the first unit.

## CONCLUSION

On the whole, this closed-circuit grinding of cement materials has been very successful, and the results have justified the installation. The plant is simple and easy to operate. Some of the requirements are stricter than in ore-dressing plants, and the results to date are highly gratifying.

## ACKNOWLEDGMENTS

Thanks are due the management of the Universal Atlas Cement Co. for permission to publish these data, and to the various members of the staff, particularly L. M. Funderberg, Superintendent, and F. P. Diener, for their care and cooperation in accumulating the information.

## DISCUSSION

O. H. JOHNSON,* Denver, Colo. (written discussion).—Mr. Counselman stated that the mills ran at approximately 75 per cent of critical speed. This I would consider on the slow side when compared with present-day ball-mill speeds employed in grinding ore. Perhaps the speeds of the mills were set to suit the lifting-bar type of liner.

I wonder if there was difficulty in balancing the work between the primary and secondary mills. On account of the kind of feed (swing hammer mill product) and the ease to grind, perhaps each mill might be able to grind to finished size.

F. R. MILLIKEN,† Salt Lake City, Utah.—In the usual grinding of base-metal or siliceous ores in two stages, if the primary and secondary grinding units are approximately the same size, in a reduction from ½ in. to 200 mesh the primary grind would be much nearer 35 or 48 mesh than 14 mesh. Admitting "mesh of grind" is far from an exact definition, there appears to be in the grinding of this material a different relation between "mesh of grind" in the primary and secondary circuits than in usual grinding practice. Is this due to particular characteristics of the materials ground?

T. B. COUNSELMAN (written discussion).—Replying to Mr. Milliken, the classification in the primary circuit was coarsened above the customary metallurgical practice, for a definite reason. There are no filters ahead of the kilns at this cement plant. Therefore, it was important to get an underflow from the thickeners with as low a moisture content as possible. To achieve this, it was necessary to minimize the overgrinding; in other words, to keep the specific surface as low as possible.

The mix at this plant includes shale, which of course slimes readily. The objective therefore was to get finished material out of the circuit as quickly as possible. The overflow dilution in the primary classifier was accordingly lowered, overflowing the finished material to the bowl classifier, where finished material was at once released to the thickener without entering the secondary grinding mill. This resulted in coarsening up the product of the primary circuit, more than would be done with an ore, where as much production as possible of minus 100-mesh from the primary circuit is desired.

---

* Vice President, Mine and Smelter Supply Co.; Manager, Marcy Mill Division.

† Metallurgist, General Engineering Co.

The relative ease of grinding this limestone and shale, as compared to Canadian gold ores, for example, answers Mr. Johnson's comments on mill speeds. Proper mill sizes, speeds, ball sizes, etc., were all worked out by accurate grindability tests, long before the plant was built, and have checked out accurately in practice. I do not think, however, that 75 per cent of critical mill speed is very far from current practice.

# 65-mesh Grinding in Closed Circuit with Stainless-steel Screens

By Walter M. Stephen*

(New York Meeting, February, 1938)

Modern developments in alloy steels have been so rapid and diverse that engineering practice has scarcely had time to re-appraise all items of past experience wherein conclusions became axiomatic under conditions that no longer apply. A case in point is the wet screening of abrasive ores within the fine range still looked upon as belonging exclusively to classifiers.

By virtue of the development of stainless steels (18 per cent Cr, 8 per cent Ni), it is no longer true that classifiers are more economical than screens in closed circuit with large-tonnage ball or rod mills at 65 or even 100 mesh, provided a selective overgrind of the higher-gravity constituents of the ore is not desired.

Wet screening of ores is a highly corrosive as well as an abrasive operation, because of the inevitably high degree of oxygenation of the water. Screen cloth of ordinary or spring-steel wire almost at once becomes pitted and covered with a film of corrosion products, which causes rust-blinding of fine-mesh screens and offers high frictional impedance to the flow of ore particles. On the other hand, the well-known properties of stainless steel enable it to maintain a bright surface, and so to eliminate blinding either by ore particles or by corrosion products.

That a large-tonnage mill grinding hard ore to 65 mesh can be operated economically in closed circuit with screens instead of classifiers has recently been demonstrated at the Copper Cliff concentrator of the International Nickel Co.; in the test to be described, a 6½ by 12½-ft. Marcy rod mill ground from 625 to 820 tons of ore per day to approximately 65 mesh, operating in closed circuit with three 4 by 5-ft. Hum-mer screens, without any classifier. Stainless-steel cloth gave an indicated life of several months. There was no difficulty with blinding, yet dilution and spray water could be controlled so that screen undersize averaged not less than 40 per cent solids. In contrast, ordinary carbon steel was pitted and blind with rust within 40 hours.

---

Manuscript received at the office of the Institute Dec. 1, 1937. Issued as T.P. 901 in Mining Technology, May, 1938.

* Assistant Mill Superintendent, International Nickel Company of Canada, Copper Cliff, Ont.

## CONDITIONS OF THE TEST

In the Copper Cliff concentrator, the crushing-plant product, finished on dry rolls in closed circuit with screens of 0.185-in. opening, is ground to flotation-feed size in a single stage of Marcy mills. At the time of the test (December 1936 through March 1937) all grinding units consisted of 6½ by 12½-ft. Marcy mills operating with rods, driven at 16½ r.p.m. by 200-hp. motors, each mill being in closed circuit with a 12 by 28½-ft. Dorr FX classifier. The flowsheet was: ore from storage bins to mill; mill discharge to classifier; classifier overflow to flotation; and classifier rake discharge back to the mill.

The test consisted of a direct substitution of the three screens for the classifier on one Marcy-mill unit, the flowsheet and all other conditions remaining the same as before. The classifier was completely shut down for the duration of the test. Performance comparisons were made against adjacent grinding units, using classifiers as usual but with no other difference in operation. The screen cloths listed in Table 1, all furnished by The W. S. Tyler Co., were tried.

TABLE 1.—*Screen Cloths Tested*

| Ton-Cap No. | Number of 4 by 5-ft. Pieces | Width of Opening, In. | Size of Wires, In. | Mesh | Wire Material |
|---|---|---|---|---|---|
| 147 | 1 | 0.0155 | 0.023–0.028 | 28 × 8 | Common steel |
| 2475 | 3 | 0.0093 | 0.018–0.025 | 41 × 10 | Stainless steel (18-8) |
| 166 | 3 | 0.0168 | 0.018–0.025 | 31 × 8 | Stainless steel (18-8) |
| 191 | 1 | 0.0110 | 0.013–0.015 | 45 × 12 | Stainless steel (18-8) |
|  | 1 | 0.0103 | 0.00975 | 50 × 41 | Stainless steel (18-8) |

*Test on No.* 147 *Ton-Cap.*—The test on the plain-steel wire screen cloth (No. 147 Ton-Cap) lasted only 40 hr. By that time the cloth was almost totally blinded by rust and had to be removed from service. None of the stainless-steel screens behaved in this way; on the contrary, all retained a bright surface throughout their operation.

*Test on No.* 2475 *Ton-Cap.*—The No. 2475 (41 by 10 mesh) gave the undersize that most closely approximated the normal classifier overflow (Table 2). The maximum capacity of each of the three 4 by 5 Hum-mers covered with the No. 2475 cloth was 210 tons of original ore per 24 hr. The screens gave approximately 30 per cent circulating load returning to the mill, as compared with a 250 per cent circulation on the classifier units, which were handling 700 tons new ore per day. Table 3 gives the screen analysis of the mill discharge, which would be the screen feed, and also of the screen oversize returning to the mill. The test of this screen was continuous for 15 days, at the end of which time there was no visible sign of wear upon the screen cloth. At no time was there any difficulty from blinding, despite the fact that there were considerable quantities of wood in the ore, which was ground fine in the mill and might have been expected to felt or mat upon the screens and blind them. Feed reached the screens at about 70 per cent solids. A light spray of water was played upon the screen at the mid-point, and another about 6 in. above the discharge. Screen undersize varied between 40 and 42 per cent solids.

Table 2.—*Comparison of Undersize with Normal Classifier Overflow*

| Mesh | No. 2475 Screen Undersize | | Comparative Classifier Overflow | |
|---|---|---|---|---|
| | Per Cent Weight | | Per Cent Weight | |
| | This Mesh | Cumulative | This Mesh | Cumulative |
| + 48 | 0.90 | 0.90 | 2.61 | 2.61 |
| + 65 | 6.38 | 7.28 | 6.21 | 8.82 |
| +100 | 12.26 | 19.54 | 10.63 | 19.45 |
| +200 | 31.24 | 50.78 | 31.13 | 50.58 |
| −200 | 49.22 | 100.00 | 49.42 | 100.00 |

*Test of No.* 166 *Ton-Cap Screen at Varying Tonnage Rates.*—The three Hum-mer screens were covered with No. 166 Ton-Cap stainless-steel cloth and operated for 33 days at varying tonnage feed rates. This cloth also showed no visible sign of wear at the end of the test, and there was no tendency to blind. Because of the wider opening, however, the final undersize product was considerably coarser. Table 4 gives a summary of this test.

Table 3.—*Screen Analysis of Mill Discharge and No.* 2475 *Screen Oversize*

| Mesh | Feed to Screens (Mill Discharge) | | Screen Oversize (Returned to Mill) | |
|---|---|---|---|---|
| | This Mesh | Cumulative | This Mesh | Cumulative |
| + 48 | 5.73 | 5.73 | 18.63 | 18.63 |
| + 65 | 10.07 | 15.80 | 19.58 | 38.21 |
| +100 | 12.13 | 27.93 | 13.22 | 51.43 |
| +200 | 27.55 | 55.48 | 20.71 | 72.14 |
| −200 | 44.52 | 100.00 | 27.86 | 100.00 |

It should be remembered that the changes in the screen undersize caused by a change in feed rate to the rod mill are due in great part to the mill itself and not to the screen.

*Test of No.* 191 *Ton-Cap Stainless-steel Cloth.*—One stainless-steel cloth of the No. 191 Ton-Cap specification was given a 48-hr. test (Table 5). This screen also operated very satisfactorily with reference to wear and absence of blinding, but the undersize product was so nearly the same as that from the No. 166 screen that the test was discontinued.

*Test of* 50 *by* 41-*mesh Stainless-steel Cloth.*—The nearly square opening of the 50 by 41-mesh screen caused rapid blinding by ore particles, so that this test had to be discontinued at the end of 36 hr. (Table 6). It was indicated that an elongated opening would have solved this difficulty. The product was finer than that produced in any previous test.

TABLE 4.—*Summary of* 33-*day Test, No.* 166 *Screen*

| Dry Tons New Ore per Day | Screen Analyses of Products, Per Cent Weight | | | | |
|---|---|---|---|---|---|
| | +48 | +65 | +100 | +200 | −200 |
| Screen Undersize | | | | | |
| 720 | 4.61 | 9.08 | 15.43 | 29.80 | 41.08 |
| 790 | 9.33 | 13.16 | 16.50 | 26.84 | 34.17 |
| 860 | 8.83 | 12.17 | 16.33 | 27.50 | 35.17 |
| Screen Oversize | | | | | |
| 720 | 39.57 | 14.01 | 13.55 | 16.68 | 16.19 |
| 790 | 53.50 | 14.66 | 10.84 | 11.66 | 9.34 |
| 860 | 60.00 | 12.66 | 10.00 | 9.50 | 7.84 |
| Mill Discharge | | | | | |
| 720 | 7.92 | 8.96 | 14.65 | 28.33 | 40.14 |
| 790 | 14.83 | 11.67 | 14.34 | 24.17 | 34.99 |
| 860 | 16.33 | 11.33 | 15.33 | 24.17 | 32.84 |

TABLE 5.—*Screen Analysis of No.* 191 *Screen Undersize*

| Mesh | Per Cent Weight | |
|---|---|---|
| | This Mesh | Cumulative |
| + 48 | 2.00 | 2.00 |
| + 65 | 7.50 | 9.50 |
| +100 | 14.50 | 24.00 |
| +200 | 30.34 | 54.34 |
| −200 | 45.66 | 100.00 |

## ECONOMIC AND METALLURGICAL CONSIDERATIONS

Since there was no sign of any considerable wear upon the stainless-steel wires at the end of 15 and 33 days, respectively, for the No. 2475 and the No. 166 screens, while the ordinary steel screen failed completely within 40 hr., it is evident that the use of stainless-steel cloth gives screens a competitive position which they do not have when using ordinary steel wire. For equal tonnages, repair cost and power consumption should be less for stainless-steel screens than for classifiers, while operating labor should be about equal. Capital cost decidedly favors screens.

In most cases, however, character of product is also an important factor. Screens necessarily make their separation according to particle diameter, independent of differing specific gravity among the several ore constituents. Unlike the classifier product, the assay of the screen product will be essentially uniform throughout its size range, if all components of the ore are equally resistant to grinding within the mill. This will be an advantage or a disadvantage, depending upon whether the grinding objective is to undergrind or to overgrind the heavier minerals. At Copper Cliff it was a disadvantage, as the ore is a mixture of heavy copper-nickel-iron sulphides and lighter siliceous gangue, and it is desired to overgrind the sulphides as much as possible, whereas a much coarser grind of the silica is permissible.

TABLE 6.—*Screen Analysis of 50 by 41 Screen Undersize*

| Mesh | Per Cent Weight | |
|---|---|---|
| | This Mesh | Cumulative |
| + 48 | None | None |
| + 65 | 1.33 | 1.33 |
| +100 | 9.67 | 11.00 |
| +200 | 32.25 | 43.25 |
| −200 | 56.75 | 100.00 |

The Copper Cliff objective is readily obtained with classifiers, the oversize in their overflow being practically barren of sulphides and therefore of little metallurgical concern. Screens could not be expected to give such a result, and did not do so. Sieve analysis of their final product showed a distribution of values practically identical with the weight distribution itself.

There are many instances in ore dressing where—unlike the condition at Copper Cliff—it is highly advantageous to be able to grind without sliming of values. This is true of gravity concentration in general, and particularly true of tin and tungsten ores. The minimizing of slime production is also important in the new and rapidly growing field of soap flotation. For applications such as these, stainless-steel screens should be ideal.

## DISCUSSION

(*T. B. Counselman presiding*)

MEMBER.—I have wondered for some time what proportion of the wear on ball and rod is due to rusting.

E. H. Rose,* Copper Cliff, Ont.—I think that every millman finds that if he shuts down a mill, or any part of the circuit that is in contact with ore, within five minutes or so there is a definite coating of rust, and within a half hour any part in contact with the ore is completely covered with rust. It must follow that the abrasion that takes place is to a very large extent the wearing off of the rust products. Of course, there is some gouging of steel—sometimes the little cuts on rods or balls can be seen—but to a very large extent it is abrasion of iron oxides.

T. B. Counselman,† Chicago, Ill.—At the plant of the Copper Range Co. at Freda, and also at Homestake, careful experiments have been made with the composition of the balls and a forged steel ball of a certain Brinell between 475 and 525 has been adopted. The ball wear has been reduced to one pound per ton very consistently, which is about the best figure of which I know. That would be a rust-resisting ball.

E. H. Rose.—We have, of course, tried out a number of alloy steels for grinding, and in all cases we have found increased life, not altogether as a function of increased hardness, but owing to the lessened corrosion.

E. L. Sweeney,‡ Denver, Colo.—What would be the results of screen sizing of this type in trying to make a product to be treated by cyanidation, using sand leaching? In other words, if the gold or silver might be dissolved in an ordinary length of time by sand leaching, would this be better for the production of that size than classification?

E. H. Rose.—I should say that a good deal more of the leachable material is in the coarser sizes and the permeability of the feed would be considerably higher. It sounds theoretically as though a very fine material ought to be easier to leach because it presents a much larger surface, but actually it is not, because the feed is not so permeable.

Member.—As I remember the circuit at your plant, the feed came into the classifier. On the screen hookup, do you run that original feed into the ball mill?

E. H. Rose.—During this test we did. That was before the bowls were replaced by the FX machines. Those were set up so that the feed could go directly into the mill, and the comparative tests on it were identical.

E. L. Sweeney.—Did you notice any difference in the action of the mills with the screen sizing as compared to the classifier?

E. H. Rose.—I would not say that we did. That is, what do you mean by action of the mill?

E. L. Sweeney.—I mean the steadiness of mill discharge.

E. H. Rose.—Are you referring to cyclic building up and unloading?

E. L. Sweeney.—Yes.

E. H. Rose.—That did not occur on the screen, of course. The process being perfectly visible, what is returning to the mill can be gauged by the eye very closely.

---

* Mill Superintendent, International Nickel Co. Mr. Rose presented Mr. Stephen's paper.

† The Dorr Company, Inc.

‡ Consulting Metallurgical Engineer and Contractor of Plants for Mines.

**Member.**—Did you change the slope of the screen in making these mesh tests?

**E. H. Rose.**—No; the slope was constant at 25°.

**T. B. Counselman.**—Mr. Rose, you have brought out that when you want selective overgrinding of the mineral the application of the screen does not work out as well as the classifier. You pointed out two or three instances where it is extremely desirable to avoid sliming of materials that must be concentrated by gravity. You have, however, made the statement that on homogeneous materials it might be highly desirable to use screens.

Probably the biggest tonnage-grinding job in the country is cement and that, from one standpoint, is a homogeneous material, but from another it decidedly is not. Even though only a cement rock is being ground, when the ultimate aim is, say, 90 per cent minus 200, would it not be desirable to obtain as much finished material as possible at each stage of grinding? In other words, if screens are used on primary grinding, a mesh sizing is obtained with practically no overgrind and minimum production of slime. The mill capacity in that primary stage would seem not to be limited if classification were used and a production of perhaps 35 per cent of finished material were obtained in that primary mill.

**E. H. Rose.**—No matter what the sizing machine is, whether it is a classifier, or a screen, or an air-separation, the rods or the balls within the mill produce the finished material, and some material will be overground in spite of anything that can be done, because some pieces are simply struck once and reduced immediately to powder if the blow is sufficient. So the production of slimes cannot be completely avoided by screening. That cannot be avoided completely, but the ratio of sizes will be better. Bureau of Mines papers were published on the various concentrators all over the United States, Canada, and Mexico. I took the screen analyses of their flotation feeds, their final grinding product, and plotted one way on the curve the plus 65-mesh as against the minus 200-mesh and located the proper point for each mill, and I found that all of those points could be joined in a smooth parabola. In some were hard ores, some soft, open circuits, single-stage, three-stage—the one thing that was in common was that they were either in open circuit or with classifiers.

The point that stood out was that no matter what was done a pretty definite ratio of minus 200 to plus 65 was obtained. That brings up the question of higher circulating loads. Those papers were published in 1930 and at that time circulating loads of 10 or 12 to 1 were unheard of. If we go back and repeat some of that work now, or observe the minus 200 to plus 65 ratio on a very high circulating load, we will find that it is materially different; there is less minus 200 and less 65 with the very high circulating load, and the screen gives almost that identical result. In other words, by squeezing the range of sizes into the center, we are making less slime and less oversize and more within the, say, minus 100 plus 200 range.

**T. B. Counselman.**—The same reasoning has been advanced against closed-circuit grinding of cement. Grinding in open circuit produces a much greater amount of "flour," as it is called in the cement industry. The cement industry is about equally divided for and against overgrinding.

We have made very careful tests of slurry produced in open circuit and closed circuit, and when the micron sizes are reached the two curves almost lie on top of one another.

You give a comparison between the screen undersize and the classifier overflow, showing approximately the same screen analysis, yet you have no measurement of the sub-sizes, so there is really no comparison of the work done by the mill.

E. H. Rose.—Our measurements were usually limited to 200 mesh; in some cases we went to 325.

C. E. Locke,* Cambridge, Mass.—One factor that was not enumerated is efficiency. We know that varies with the capacity and we know that there is apparently a limit to the efficiency of classifiers. I would assume that screens were susceptible of getting higher efficiency. Were any measurements made to determine the relative efficiency in terms of purity of the oversize? You say that it is substantially the same as far as the finished product goes. How about the sand returns?

E. H. Rose.—That is covered in the paper. Table 3 shows the screen oversize on the No. 2475 screen. The cumulative on 100-mesh was 51 per cent of the total weight of material returned to the mill. The remaining 48 per cent or 49 per cent was undersize; but on that screen there was only 30 per cent of the total returning to the mill, anyway. So the actual tonnage of unfinished material returning to the mill was very low, and to work out an efficiency on that circuit it would be necessary, of course, to take that into account.

The circulating load on the classifier would have been increased, and I think that could not be done on the screen. That is a feature of the classifier that does not apply to the screens. I do not think it would be possible to build up a circulating load on the screens. The material would either go through or it would not. Very quickly the screens would be covered so that the loads could not get down to the meshes to get through; they would never be presented to the mesh openings at all on large amounts.

C. E. Locke.—That would mean, then, that the screen has the possibility, if it is desirable, of getting a higher efficiency.

E. H. Rose.—Yes, provided the screen is not overloaded.

C. H. Benedict,† Lake Linden, Mich.—With copper ores containing metallics there is a problem introduced different from those with a sulphide. What blinding would there be on screens? It probably shows up to some extent in grinding gold ores, although metallic gold in the ore is very fine.

E. H. Rose.—I would be afraid to predict on that. Possibly the malleable constituents would. One thing that did come out in our test is that the square-mesh opening cannot be used. The elongated type of opening blinds much less readily.

E. J. Roberts,‡ Westport, Conn.—In Table 2, the products are practically identical except on 48-mesh. One is 610 tons and the classifier was doing about 700 or 750, and yet the screen oversize returned to the mill is dirty—that is, 38 per cent plus 65, or only 18 per cent plus 48—and the mill discharge is fairly fine. Yet that much grinding—600 tons—is obtained with only a 30 per cent circulating load as against 250 per cent load with the classifier. It seems as though the increased circulating load of from 30 to 250 per cent ought to give more than that 100 tons difference because the rake product of the classifier at a 250 per cent circulating load would be much coarser than the screen oversize.

T. B. Counselman.—I want to ask Mr. Rose a question. Mr. Maxson brought out§ that a certain amount of work is done for every revolution of the mill, more or less, regardless of the way of doing it. Referring back to information that we have gathered from various operations, we have arrived at a more or less "rule of thumb" measure of what a mill capacity ought to be.

---

* Professor of Mining and Ore Dressing, Massachusetts Institute of Technology.

† Metallurgist, Calumet and Hecla Consolidated Copper Co.

‡ The Dorr Company, Inc.

§ See page 310.

For instance, in grinding to 48 or 65 mesh, we find that a mill should be able to grind somewhere between 9 and 14 tons per day per cubic foot of mill volume. That means the total through the mill, circulating load plus original feed. If that is correct, it leads to something very interesting. With the 250 per cent circulating load and about 750 tons going through the mill, the throughput of the mill is only about 5 tons per cubic foot, which may be explained by the hardness of the ore, or some other reason. With a screening operation, with a 30 per cent circulating load (and I use the same tonnage here), there is 2.6 tons per cubic foot. On that basis the mill ought to do much more, and the question I want to ask is whether you have looked into that at all, and whether you think that by close-circulating with enough screens you could push the mill capacity higher than you could do it with classifiers?

E. H. Rose.—That I cannot tell you. The mills at the time of the test were running at 18½ r.p.m., and we have since speeded them up to 24 r.p.m., and have put on a peripheral discharge grate—originally we had a 38-in. discharge. We put on a discharge grate, and increased the size of the motor, and those mills are now putting out 1200 tons per day of finished material.

T. B. Counselman.—If you were to close-circuit a mill with enough screens to do a certain job and get a certain desired result, would you not be introducing too many complications in the way of distributing the feed and collecting the products, particularly the oversize of the screens, to return this back into the mill? The simplification of the classifier is decidedly worth while.

E. H. Rose.—It is true that it is not necessary to distribute the feed on the classifier for several units, at least most standard ones. It does all go to one classifier; the one classifier can be large enough to do the whole job in one machine. That is definitely a factor as against the screens.

However, the total capital cost is somewhat less—the power and operating costs are about the same or possibly a little less. The thing hinges a great deal on the type of product desired. If you must have dimensional sizing, the classifier cannot give it unless the constituents are of the same gravity.

The whole business of fine-screening is definitely limited to certain applications, as I say. That is witnessed by the fact that even after the tests we did decide upon classifiers.

T. B. Counselman.—You say that you ran these stainless-steel screens for as long as 33 days and could observe no particular wear. The factor on the wear that would be serious would be enlargement of the opening, changing the mesh of grinding. You have no information at all as to how frequently you would have to replace your screens in order to maintain the desired mesh?

E. H. Rose.—No, I have not. We did not carry any of the tests to the point of actually wearing out the screen. Of course we took daily screen analyses of the product and we did not see any progressive increase in the size of the screen product. There was no measurable increase in the 30-day period.

T. B. Counselman.—Would not stainless-steel screens, in the last analysis, prove expensive on upkeep on that account?

E. H. Rose.—No, they would not; in fact, they would effect an economy in upkeep and repair as compared to the ordinary wire screen. In spite of the fact that they are somewhat higher in price, the capacity per square foot is also much higher, so that the longer life in a sense could be considered as a saving.

T. B. COUNSELMAN.—I am thinking of the classifiers, of course.

E. H. ROSE.—That would depend very largely on the individual job. I can see how in some cases it might be more and in others it might be less.

N. L. SHEPARD,* East St. Louis, Ill.—Our screens have a life varying anywhere from 18 hr. to over a month and the wear is always where the rubber backing-strips on the supporting deck—about a 4-mesh there—touch the screen surface. When a screen wears out the pattern of those cords is always worn into the screen. We often increase the life by soldering the first breaks by means of the blow torch, without removing the screen.

T. B. COUNSELMAN.—That checks with my own experience. We tried to do some commercial screening on 100-mesh screens and when the screen was worn out, it had just been worn through from the underside by the supporting strips.

Another thing that we found (Mr. Davis worked on this) is that on any screening job the capacity of a screen is determined primarily by the ability of the particles to penetrate the surface of the film of water running down the underside of the screen. That is of paramount importance, and in fine-screening it becomes a pretty vital factor.

E. H. ROSE.—We did not meet that difficulty. In fact, we all know that a dry 200-mesh screen will hold water.

E. H. ROSE (written discussion).—A second, similar test of fine screens is planned here for the fairly near future. The first test was admittedly incomplete, but it did show that the use of stainless-steel wire puts a very different aspect upon fine screening. In the next test, we hope to secure considerably more extensive data, including figures on ultimate life of cloth.

---

* Research Chemist, Aluminum Research Laboratories, Aluminum Ore Co.

# The "Electric Ear," a Device for Automatically Controlling the Operation of Grinding Mills by Their Sound*

By Harlowe Hardinge,† Member A.I.M.E.

(New York Meeting, February, 1939)

The sound made by ball, pebble and rod mills has long been used by the operator as the "telltale" of their operation. The nature of this sound depends upon local conditions and the type of mill used. By experience an operator can tell whether the mill is running properly or not. Some operators are able to detect the difference in sound much better than others and get better results running the same mill under the same conditions.

The automatic operation of a mill using sound as the fundamental means for maintaining control presents many problems. The satisfactory solution of these problems requires, for given operating conditions, a greater average output, with improved product for subsequent processing, than can be obtained by manual control.

## Relation of Sound to Useful Grinding Energy

Experience has taught us that there is a difference in character as well as in intensity of sound between a mill grinding wet and one grinding dry, in open or closed circuit, to obtain a coarse or fine product, on the same material, to say nothing of the effect with a variety of different materials. Broadly speaking, a wet-grinding mill operates best at a lower sound level than the same mill grinding dry, with other conditions the same. Several reasons for this variation in sound intensity under these conditions can be advanced, but the important point is that there is a difference, based upon practical results. Since these reasons may be more or less involved, and may be subject to much discussion, only one will be considered here. It is apparent that two balls hitting together or a ball striking the lining, if there is no intervening material, will produce the maximum sound. If a complete cushion of material is placed between the balls or ball and liner, so that the energy is dissipated without doing useful work, the balls will be unable to create enough pressure or force to fracture the particles, and the sound will be at a minimum. At some point in between—that is, where there is sufficient material between the balls or ball and liner so that the ball will fracture the particles without mashing them unduly—the sound

---

Manuscript received at the office of the Institute Jan. 7, 1939. Issued as T.P. 1076 in Mining Technology, July, 1939.

* The name "Electric Ear" is a trade mark, registered at the U. S. Patent Office.

† President and General Manager, Hardinge Company, Inc., York, Pa.

with relation to the grinding effect will register the best grinding efficiency. In any ball mill it is impossible, of course, to obtain an ideal grinding action throughout the mill, where the ball just crushes the particle without overgrinding it, but there is some best average noise level where this action takes place, or where there is a greater number of proper impacts of ball against ball, or ball against liner, than at any other noise level. Fig. 1 illustrates this point.

A change in feed size, all other conditions being constant, causes a variation in the noise level, as this alters the spacing between the balls or ball and liner, but since a certain noise level is indicative of optimum grinding within the mill, unless the feed rate is changed to match this new condition, the noise level will be different and the mill will then fail to operate at the maximum grinding efficiency.

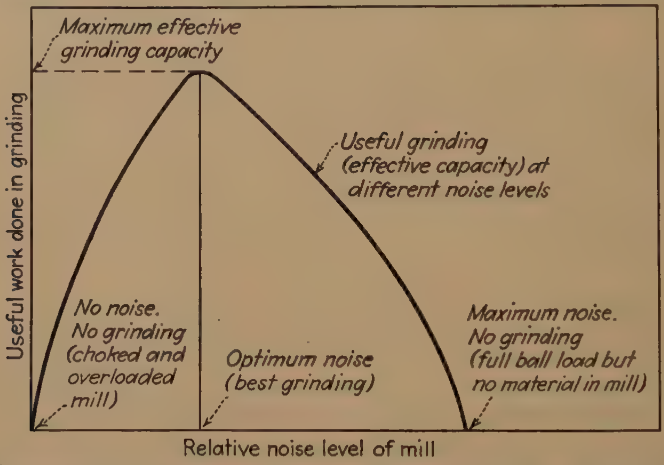


FIG. 1.—RELATION BETWEEN NOISE LEVEL IN MILL AND USEFUL WORK DONE IN GRINDING. Note that there are two noise levels for any one grinding rate, except the optimum.

If the feed size and material to be ground do not change, but a different fineness is desired, it follows that, in open-circuit grinding at least, a different noise level produces another product. A higher noise level or louder mill, all other conditions being equal, should produce a finer product, as this means that the balls are closer together and hit through the individual particles of material, producing a finer product, with a tendency to overgrind. Conversely, a lower noise level means that the balls are farther apart, the blows are somewhat cushioned, since there is less mashing action or tendency to overgrind, and a coarser product is produced, providing the material is allowed to flow freely from one end of the mill to the other, as in the ordinary continuous grinding mill. When the balls are spread apart, the volume in the mill is greater, the rate of flow through the mill is faster and a coarser product should result also on this account, since the balls have less of an opportunity to hit a particle.

In closed-circuit grinding, the rate of passage through the mill has an effect upon the number of blows the balls could give to an individual particle and the chances of its being underground or overground. Therefore, for a constant noise level, the fineness may be changed considerably by controlling the circulating load without departing from reasonably efficient operation. In other words, when grinding in open circuit, if the sound level of the mill is changed, the fineness of product changes and also the capacity, but in closed-circuit grinding it is possible to maintain a constant fineness even when the noise level is changed, or the fineness may be altered and the noise level maintained constant. However, there is an optimum noise level for any fineness, even in closed-circuit grinding, to obtain most efficient results.

This should not be confused with the relation of sound to capacity for any given fineness of product delivered from a mill grinding in closed circuit, or the effect of a change in sound level on the fineness at a given capacity under the same conditions. The relation of sound to grinding efficiency—effect on capacity or fineness or both—in practice has been found to be very pronounced, so much so that even a slight change in sound intensity—less than that which can be detected by the human ear—makes an appreciable change in capacity, as will be shown later.

## Sound Intensity and Frequency Measurements

In order to determine the actual quantity of sound produced, and whether frequency or pitch has any relation to conditions within the mill, a test was made using a conical ball mill 5 ft. in diameter with a 36-in. cylinder, grinding a hard, brittle sinter dry, in closed circuit with a reverse-current air classifier, to a fineness of about 90 per cent minus 200 mesh. The mill was run under different conditions: (1) with virtually nothing in the mill except balls, (2) with the mill three-fourths loaded, (3) fully loaded and (4) overloaded. A BTL D-94919C sound-level meter and D-95970 frequency analyzer* were used in making the measurements. The microphone was placed approximately one foot from the feed cone at a point approximately two feet below and slightly to one side of the vertical axis of the mill on the "down" side. Fig. 2 shows the results.

The sound intensity increases with a decrease in mill loading, which occurs for all frequencies. The extremely high frequencies are erratic and complex in their response, but since these high frequencies show a falling off in intensity over that of the middle range or normal frequencies, any erratic tendencies here would not be factors in registering an average noise-intensity level throughout the entire frequency range. The curves show that the intensity levels of the frequency components shift relatively uniformly with the change of load in the mill, within the middle frequency range particularly. It is interesting, and important in practice, that no particularly prominent frequencies occur that might serve to distinguish one load condition from any other; and, furthermore, by using a method of sound pickup that is most sensitive in the middle frequency range, a quantitative measurement of sound intensity issuing from the mill can be obtained without encountering any bad effect or faulty operation due to variations in frequency.

---

* Experimental models of equipment built by Bell Telephone Laboratories.

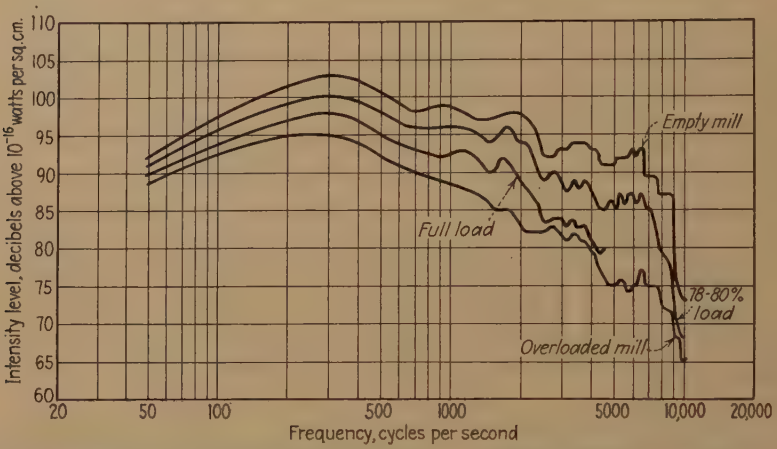


FIG. 2.—FREQUENCY ANALYSIS OF NOISE MADE BY 5-FOOT BY 36-INCH HARDINGE BALL MILL OPERATING UNDER DIFFERENT LOAD CONDITIONS.

## PRACTICAL CONSIDERATIONS OF SOUND CONTROL

A device that utilizes the intensity of sound to control the operation of a grinding circuit must meet a number of requirements to produce the results desired. It must, in effect, take the place of the operator's ear and be able to control mechanically, as the operator does by hand, the rate of feed or other factors that affect the operation of the grinding circuit. It should be strong mechanically and reliable electrically. A ready means of regulation without limiting its ability to control the grinding circuit under all ordinary conditions is a requisite. A method should be incorporated that permits the operator to change the noise level at will to control capacity, fineness, etc. The device should also be able to confine the noise level of the mill within narrow limits. These limits should be held much closer than those possible of detection by the human ear. Installed first cost and operating cost should be reasonable. Installation should be possible with little if any interruption to operation. The unit should be so constructed that it can be used on different types of mills under different grinding conditions. These comments are offered because often a device that shows promise fails because it is workable only in the laboratory or under more or less ideal conditions.

## THE "ELECTRIC EAR"

### *Construction*

The "Electric Ear" comprises a cabinet containing an electrical control circuit, an operating control panel and a microphone.

The microphone is at the focal point of a parabolic reflecting shield in which it is suspended. This increases the intensity of the sound from the mill picked up by the microphone and eliminates extraneous noises from other mills and equipment near by. The front is covered with a fabric to exclude dust and moisture. The back is covered by a soundproof housing. This assembly is placed near the mill adjacent to a point at which the balls strike the lining.

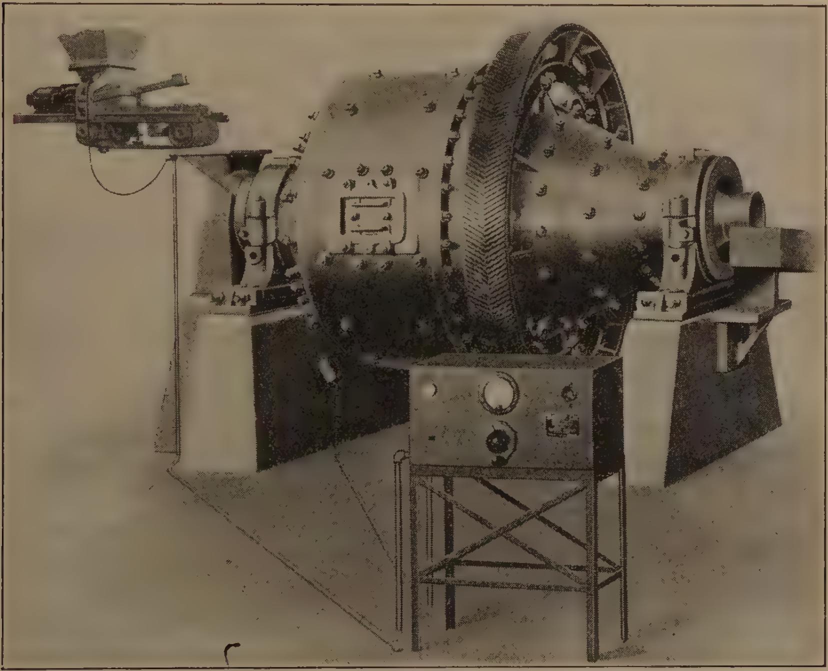


FIG. 3.—TYPICAL ARRANGEMENT OF "ELECTRIC EAR," MILL AND FEEDER.
Microphone under mill picks up sound, which is converted into electrical energy in control cabinet. Energy is utilized to actuate feeder, so mill conditions are held constant at any desired noise level.

The cabinet houses the electrical equipment and power relay for controlling a feeder and other auxiliary mill equipment from the sound energy received by the microphone. A time delay relay prevents "fluttering" or momentary changes when the noise fluctuates excessively at short intervals. The cabinet may be installed at any convenient place in the building.

The control panel, which forms the front of the cabinet, has mounted upon it an indicating microammeter, a sound-level regulator and two pilot lights. The microammeter provides a relative measure of sound energy. The sound-level regulator is calibrated so that the relative sound level may be indicated. One pilot light indicates the power supply to the control system and the other the power supply to the equipment being controlled.

For a fixed position of the indicator on the noise-level regulator an increase in the reading of the microammeter represents a higher noise level. A decreased microammeter reading accompanies a lower noise level. The "Electric Ear" functions as a sound-level meter under these conditions. The actual operation of the "Electric Ear" requires a constant reading of the microammeter and positions of the pointer on the sound-level regulator dial are representative of different noise levels.

Units have been constructed and operated using amplifiers. Other arrangements have been employed to control variable-speed motors for speeding up and slowing down the feeder, but it has been found that, for most purposes at least, these refinements are unnecessary. It is then possible to use a much simpler and more foolproof unit. Fig. 3 illustrates the arrangement of the various parts in a standard grinding circuit, consisting of feeder, mill, microphone and control box. There is a sensitive control circuit inside the cabinet, which operates at one current intensity only. It is this circuit that is affected by the noise-level regulator or by a change in noise level coming from the mill. This circuit in turn actuates the power switch, which operates the feeder.

## *Operation*

Before the "Electric Ear" is connected to the feeder but after it is set up and the control circuit energized so that it will register the noise of the mill, the dial of the intensity regulator is adjusted so that the meter reads, say, 35 microamperes, which, for the sake of explanation, we will assume to be the current required to operate the feeder relay circuit. We then leave the unit alone and observe the change in relative sound intensity that occurs when the mill is operated manually in the ordinary way. The meter reading probably will vary from as low as 20 to as high as 60 microamperes over a period of a day, even though the mill is operated "correctly" by the operator and never overloaded or underloaded, according to his judgment. Even greater variations than this sometimes occur without observation by the operator, when he is moving about the building and is not watching the mill closely. In other words, his impression from one hour to another of what he might consider the same noise level or proper operating load would not coincide at all with the quantitative measurements as recorded by the meter.

When the "Electric Ear" is ready to be connected to the feeder circuit, the usual practice is to open the feeder motor circuit, or the remote-control relay circuit in the feeder switch circuit and connect in the power switch of the "Electric Ear." The feeder will then operate only when the power switch of the "Electric Ear" is closed, which closes the feeder power circuit. When the power switch is open the current in the feeder circuit is broken and the feeder stops.

At the time the power switch of the "Electric Ear" is connected into the feeder circuit, the feed rate is immediately stepped up 20 to 30 per cent above the previous normal. The mill seldom need be shut down to make this connection and change, as usually it can be done in a few minutes. Since the feed rate is then in excess of normal, the mill begins to quiet down, which decreases the energy picked up by the microphone. The meter reading shows a slight decrease, perhaps 1 or 2 microamperes, and the power circuit opens, which stops the feeder. The noise level starts to rise when the feed is off, and when the current in the control circuit increases above the so-called cutoff point of 35 microamperes the power relay closes and the feeder starts. The circuit is so sensitive that in normal operation the unit starts and stops at plus or minus 35 microamperes, and seldom more than 2 microamperes difference instead of the 20 or 30 microamperes, which is the range of "good" hand control.

Under normal conditions the feeder is shut off anywhere from 2 to 20 sec. and the "on" period is proportionately longer—that is, from 10 sec. up to 1 min., except when there is a change in characteristics of the feed; then there is a considerably longer period between changes, until the mill is adjusted to the new condition of feed. The "on" and "off" periods of feed seem to be quite consistent regardless of the size of mill. The 12-in. laboratory mill, requiring ¼ hp., operates on the same time cycle as a 10-ft. mill taking 500 horsepower.

Since there is only one adjustment on the "Electric Ear," the sound-level dial pointer, movement of this pointer is the means employed to change the noise level to any desired amount. By operating the mill at different noise levels, the operator determines the best grinding conditions, not possible of attainment otherwise, as will be shown in curves described later. Short on and off periods have an advantage over long periods. Wide fluctuations in the grinding circuit are minimized and a simple method of starting and stopping the feeder may be employed rather than requiring the use of a variable-speed drive, or slow and fast motor.

Fig. 4 shows a chart of a recording ammeter in the feeder motor circuit controlled by an "Electric Ear" on a 10-ft. Hardinge ball mill grinding limestone to a fineness of about 90 per cent through 200 mesh, at the plant of the North American Cement Co., Hagerstown, Maryland. The mill is in closed circuit with an air classifier. Analyzing this chart, it appears that the character of the feed remained fairly constant from 3 p.m. until shortly after 7 a.m. An arbitrary change in the fineness of the product was made on this day between 7 a.m. and 3 p.m., which shows up very strongly on the chart. From about 3 p.m. to 8 p.m., the feed must have been reasonably uniform, as the on and off periods were fairly regular. After that time, owing probably to a difference in the grindability of the feed, there was a considerable change in the on and off period. During this same period, there must have been a harder grinding material, as indicated by an increase in the off periods. Probably the conveyor feeding the mill bin was not running, the bin "coned" down and the feed then contained less fines and the mill could not grind as much. At midnight another change occurred, variations taking place from then on up to 7 a.m., probably caused by bin segregation where coarse material along the outer edges of the bin would slide down from time to time, causing a variation in the grindability of the stone at those times. An excellent example is afforded here, which shows what occurs during the course of a day and how difficult it is for an operator, no matter how good he may be, to control a mill to the best advantage.

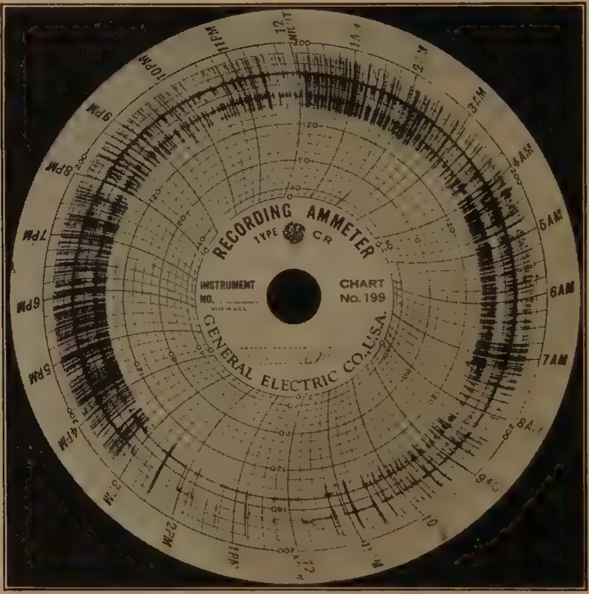


FIG. 4.—RECORDING CHART SHOWING "ON" AND "OFF" PERIODS OF FEEDER OF 10-FOOT CONICAL BALL MILL, GRINDING LIMESTONE, FROM ½ INCH TO 90 PER CENT MINUS 200 MESH.

Note how running periods varied during course of a day, owing to changes in hardness, size of feed, bulking, bin segregation, and other causes.

### *Fields of Usefulness of Sound Control*

The "Electric Ear" has controlled various types of mills under a wide variety of grinding conditions. In the wet-grinding field it is controlling mills grinding in open circuit and in closed circuit with classifiers, from 12-in. diameter ball mills to 10-ft. ball mills. It is being used with wet-grinding rod mills and tube mills also. In grinding dry it is operating with ball, pebble and tube mills in closed circuit with air classifiers and screens, as well as grinding in open circuit.

The "Electric Ear" has been applied also on mills grinding coal. In one instance the output of the coal pulverizer was the controlling factor, in that the rate of discharge of coal from the mill was changed at the burner, not at the mill. This change was made by varying the quantity of air permitted to flow through the mill. When the quantity of coal removed was increased, the noise level increased. The "Electric Ear" that controlled the feeder would then add more feed to bring the noise level back to normal. Conversely, when the supply of coal to the burner was reduced, the mill would tend to load up slightly, and the feeder would stop oftener to keep conditions constant within the mill.

The "Electric Ear" has also been used as an indicator of mill loading only. In observing the sound intensity as registered by the meter, the operator alters the feed or changes the mill control by hand.

### *Open-circuit Grinding*

As mentioned in the first part of this paper, the behavior of a mill controlled by the "Electric Ear" grinding in open circuit differs somewhat from that when it is grinding in closed circuit, either wet or dry. Fig. 5 shows what occurs when the mill is controlled by the "Electric Ear" grinding dry in open circuit.

Starting with a mill of normal ball charge, but without feed, there is, of course, no capacity. Under these conditions the sound-intensity dial setting of the "Electric Ear" was 55 for a mill full of balls but without material to be ground. This represents a high relative noise level. The control dial was then turned to 50 and a test made at that point. A moderate decrease in sound level produced a marked increase in the capacity. Other tests were made at different sound levels, approaching a quieter mill. Maximum capacity was reached between the reading of 35 and 40 on the dial and the amount of minus 65-mesh in the product did not change greatly between these points. As the test continued, with a quieter mill, the capacity dropped off rapidly until just under 25, when it increased just as rapidly, while the amount of minus 65-mesh in the product, as well as the percentage of minus 65-mesh in the product, fell off also very rapidly. This increase in the total feed rate rather than a continued decrease might be considered an unexpected result, but it is not, if we consider that the mill becomes overloaded in decreasing the noise level in stages by resetting the "Electric Ear" each time. As soon as the "Ear" is reset to a quieter level, the feeder remains on for a few minutes to quiet it down. In an overloaded mill the balls become spaced and the grinding efficiency falls off rapidly, and eventually a point is reached at which almost no grinding is being done; if feeding is continued, the mill then acts as a conveyor, and beyond a certain low noise level the material floods out of the mill in an underground state, equal to the feed rate. The gross output increases but the actual grinding rate decreases.

The mill is sensitive to a small change in sound level and the point of maximum capacity shows up as a sharp peak, which should explain in a measure why the use of sound as a controlling medium permits the mill to be operated at higher capacity than is possible by manual control, since the operator is unable to keep the mill running even within 10 to 20 points of the relative sound level during a day's time.

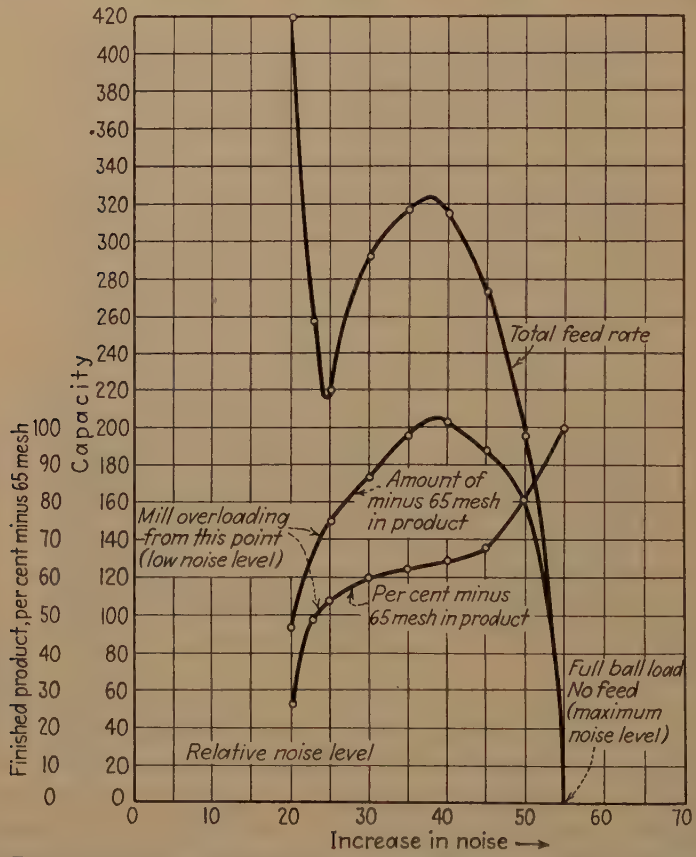


FIG. 5.—RELATION OF NOISE LEVEL TO TOTAL FEED RATE, AMOUNT OF FINISHED PRODUCT OBTAINABLE, AND FINENESS IN MILL GRINDING IN OPEN CIRCUIT.

In open circuit, the fineness varies with a change in sound level. With a noisy mill the fineness increases rapidly, but during intermediate noise levels the increase is more gradual and then falls off rapidly again as the mill becomes too quiet or overloaded. In the case under consideration here, it happens that maximum capacity occurred at a fineness of 63 per cent minus 65-mesh. If it is desired to operate the mill at, let us say, 50 per cent minus 65-mesh, we would be at or near the point of overload, all other conditions remaining the same, but inasmuch as this grind is coarse, the remedy would be to change the feed size or change the size or quantity of the grinding media or both to obtain maximum or near maximum capacity at the fineness desired. Thus by the use of sound as the regulating medium, best grinding conditions can be secured for a given specification by making a series of tests and establishing the optimum point. These tests can be conducted systematically and not by cut and try methods.

### *Closed-circuit Grinding*

The effect of sound on fineness when grinding in closed circuit, either wet or dry, is not so pronounced as when grinding in open circuit. Grinding factors within the mill can be controlled much better when the mill is operating in closed circuit, for then the rate of flow through the mill may be altered considerably, without affecting the fineness noticeably. For a given sound level the fineness may be changed by varying the circulating load and the sound level may also be altered and yet the fineness held practically constant. Since the sound level is an indicator of grinding efficiency, as already pointed out, if the sound level is altered and the fineness is kept constant, a new method of regulation is available. This method offers extensive opportunity to increase grinding efficiency beyond that attainable heretofore, irrespective of the advantage of such a system in maintaining conditions constant, once the best point of efficiency has been established. The results attained by the International Nickel Co. through the use of the "Electric Ear" described later on in this paper illustrate the method employed and the advantage of using sound as the controlling element in a closed-circuit grinding system.

### *Control of Density*

When grinding wet in open or closed circuit, the control of density has always presented a problem, since a change in density not only materially affects the grinding circuit itself but often the subsequent process. A simple means has been devised to maintain the density constant within the grinding circuit when using the "Electric Ear." The method maintains the density constant at the outset instead of correcting a change in density after it has occurred. If the mill is fed with a weighing type of feeder and the operation of this feeder is controlled with the "Electric Ear," and at the same time water is supplied to the mill from a constant head source and controlled simultaneously with the feeder, the ratio of water to solids is maintained constant and by weight, which means maintaining a constant density. To accomplish this result, electrically operated valves are placed in the circuit, so that when the "Electric Ear" shuts off the feeder the water to the system is shut off simultaneously, or if the feed is reduced to half, let us say, the water is also cut in half, still maintaining a constant density.

In order to smooth out the operation, the water can be fed to a surge tank, the head in which governs the supply of water to the mill corresponding with the average rate of feed. In other words, when the grinding rate is reduced by the feeding of hard or coarse material the feed rate is automatically reduced and simultaneously the water supply to the surge tank is reduced in proportion, which will lower the average head in the surge tank and lower the average rate of supply of the water to the mill or classifier, or both, in exact proportion.

Modifications of this principle of density control have also been used where volumetric feeders have been employed and to control part of the mill circuit only, with good results and without the use of a surge tank, particularly when the dilution of the mill only is controlled and the classifier dilution is regulated by hand, if and when this is needed.

### *Practical Limitations of Use*

The "Electric Ear" can be used to control the mill operation automatically only where it is possible to control the feed to the mill directly or indirectly through its own operation. In other words, if the feeder is driven by belt, chain or other mechanical means, an electrically operated clutch, ratchet or pawl must be installed so that the feeder can be actuated directly by the "Electric Ear."

Where a mill is fed from another source, and there is no regulating feeder such as a regrinding mill, and where there is no chance for controlling the rate of feed to this mill, the successful application of the "Electric Ear" is doubtful, unless the feeder of the primary mill can be controlled by the sound from the secondary mill, by using a modified method of control.

Where two mills are operated in closed circuit with one classifier and the oversize from this classifier is returned to the two mills, the operation of the "Electric Ear" is unstable, as it is practically impossible to make sure that the oversize discharged from one mill is returned to that mill and not to the other mill. There are other combinations that offer difficulties along similar lines.

For best operation and best results, the conventional arrangement of feeder, mill and classifier, all functioning as one unit, makes the best arrangement. In this circuit it is advisable that any conveyor leading from the feeder to the mill, if it is very long, be stopped and started along with the feeder, so as to prevent an unduly long lag between the time at which the feeder stops and that at which the feed entering the mill from the long conveyor stops flowing. This applies also where the feed enters the classifier first. The time lag in this case should be shortened as much as possible, or a modified form of variable-speed drive on the feeder can be employed to advantage.

While "Electric Ears" are controlling a wide range of operations in many fields, there still remain combinations to be worked out to the best advantage. It is interesting, however, in analyzing the results, to see the close relationship that exists between sound and grinding efficiency. There has been so much to learn about this principle of control that to describe its operation publicly prior to the present time was thought inopportune, even although the early units constructed in a rather crude way are still running.

## OPERATION AND TESTS OF "ELECTRIC EAR" BY INTERNATIONAL NICKEL COMPANY

In April 1938 the International Nickel Co., Copper Cliff, Ontario, installed an "Electric Ear" on what is known as the No. 17 mill.

The No. 17 mill is a peripheral discharge ball mill, 6½ ft. in diameter by 12½ ft. long, running at 23.1 r.p.m. At the time the "Electric Ear" was installed, a series of tests had just been conducted, in which the mill was operated under various conditions to determine the best operating efficiency. The mill is in closed circuit with a 12-ft. Dorr FX classifier. The feed to the mill is all through the equivalent of a 3⁄16-in. mesh screen, delivered to a bin by a shuttle conveyor and discharged by six pocket roll feeders, three feeders being used at a time, in an effort to obtain uniform feed to the mill. The "Electric Ear" was put into operation without connecting it to the feeder motor. Numerous readings of relative noise level were taken to determine the so-called cutoff point at the conditions of operation. Readings taken over a period of a day during the time the operator controlled the mill in the usual manner indicated that he maintained a noise level varying to the extent of approximately 12 points on the sound-level dial, or, as it is called by International Nickel Co., "tone-dial setting." The unit was then connected to the feeder circuit and the feeder speed was increased about 30 per cent. A few minutes thereafter the "Electric Ear" began to cut off the feed in the usual manner. After several days preliminary test work the "Electric Ear" was set at a tone-dial setting of 76 and the test commenced at this setting.

The tonnage reported for the period of Feb. 22 to 28 without the "Electric Ear" averaged 1182 tons per day at 14.82 per cent plus 65-mesh. The average tonnage for the month of March was reported as 1127 tons at 14.99 per cent plus 65-mesh, the power average for the month of March being 5.29 kw-hr. per ton. The best 8-day average, from March 1 to March 8, was reported as 1144 tons at 15 per cent plus 65-mesh, the power being 5.12 kw-hr. per ton.

The "Electric Ear" was operated for about 10 days prior to taking full test data, during which time an attempt was made to determine the best noise level to operate the mill under the existing conditions. The tone dial, or as we call it, the sound-intensity regulator, was finally set at 76 during the first period of April 26 to May 5, with a resultant tonnage of 1270 tons at 14.64 per cent plus 65-mesh. A series of careful tests was then conducted, ranging from 4 to 11 days each, with different settings of the tone dial. The data are summarized in Table 1. A curve was drawn to determine the effect of sound on mill capacity, prior to the last test conducted in July 1938. From this curve it appeared that the apparent optimum noise level was somewhere between the setting of 80 and 76. Another test was conducted from July 7 to July 20 at a dial setting of 78, and the best results of all were obtained; namely, 1304 tons at 14.98 per cent plus 65-mesh.

TABLE 1.—*Copy of Summarized Data Sheet on No. 17 Ball-mill Unit as Equipped with the "Electric Ear," International Nickel Co., Copper Cliff Concentrator*

| Date, 1938 | Apr. 26–May 5 | May 6–10 | May 22–28 | June 1–4 | June 6–10 | June 12–18 | June 19–26 | July 7–July 20 |
|---|---|---|---|---|---|---|---|---|
| "Electric Ear" tone-dial setting | 76 | 80 | 80 | 70 | 70 | 83 | 60 | 78 |
| Dry tons per 24 hr | 1,270 | 1,324 | 1,254 | 1,193 | 1,170 | 1,178 | 1,104 | 1,304 |
| Horsepower input | 334 | 334 | 333 | 339 | 335 | 330 | 335 | 342 |
| Kilowatt-hours per dry ton | 4.71 | 4.51 | 4.75 | 5.08 | 5.12 | 4.91 | 5.43 | 4.69 |
| Percentage sulphur in feed | 14.4 | 15.8 | 14.2 | 14.9 | 14.2 | 15.1 | 14.4 | 14.9 |
| Classifier overflow, per cent: | | | | | | | | |
| Solids | 38.62 | 39.30 | 36.75 | 37.50 | 36.40 | 37.10 | 37.90 | 41.70 |
| +65-mesh | 14.64 | 14.63 | 14.72 | 13.04 | 13.46 | 13.16 | 11.69 | 14.98 |
| −200-mesh | 49.16 | 51.60 | 49.16 | 50.85 | 49.60 | 51.40 | 51.23 | 50.22 |
| Mill discharge, per cent: | | | | | | | | |
| Solids | 83.3 | 83.3 | 83.2 | 83.1 | 82.1 | 82.2 | 81.6 | 83.7 |
| +65-mesh | 52.34 | 59.05 | 59.14 | 55.99 | 52.72 | 55.40 | 49.98 | 53.74 |
| −200-mesh | 21.06 | 17.88 | 15.08 | 16.97 | 19.02 | 17.96 | 21.20 | 19.27 |
| Mill feed, per cent: | | | | | | | | |
| Moisture | 2.09 | 2.10 | 1.97 | 1.99 | 1.81 | 1.94 | 1.88 | 1.84 |
| +65-mesh | 68.82 | 70.84 | 72.74 | 69.94 | 68.31 | 70.89 | 69.90 | 69.19 |
| −200-mesh | 17.70 | 16.56 | 15.30 | 16.02 | 17.12 | 17.47 | 17.19 | 17.36 |
| Circulating load, per cent | 273 | 363 | 454 | 297 | 323 | 356 | 278 | 341 |
| Number of days in test period | 10 | 5 | 7 | 4 | 5 | 6 | 6 | 11 |
| Test period No | 1 | 2*a* | 2*b* | 3*a* | 3*b* | 4 | 5 | 6 |

Fig. 6 shows the graph obtained as a result of the test work. It is interesting to see how much the capacity changes for a relatively small change in noise level at or near the most efficient grinding rate, a factor of considerable importance when it is realized that the best an operator can do is keep the mill within 10 to 15 points of the noise level as indicated here. Also the capacity falls off rapidly on the "quiet" side of the curve. In other words, to hold the mill at maximum capacity, the operation must be held within very close limits; otherwise the mill will overload quickly when it is only a little "too quiet." This may explain in part why the "Electric Ear" is able to increase capacity so much over that of a manually controlled mill. It was thought before the tests were commenced that there might be steadier operation, but not much of an increase in capacity over the manually contrólled mill, owing to the relatively fine feed, the excellent distribution in the bins, the fact that three feeders were used simultaneously, as well as the close control of conditions in this entire mill generally, owing to excellent supervision. The increased capacity attained was much greater than was expected.

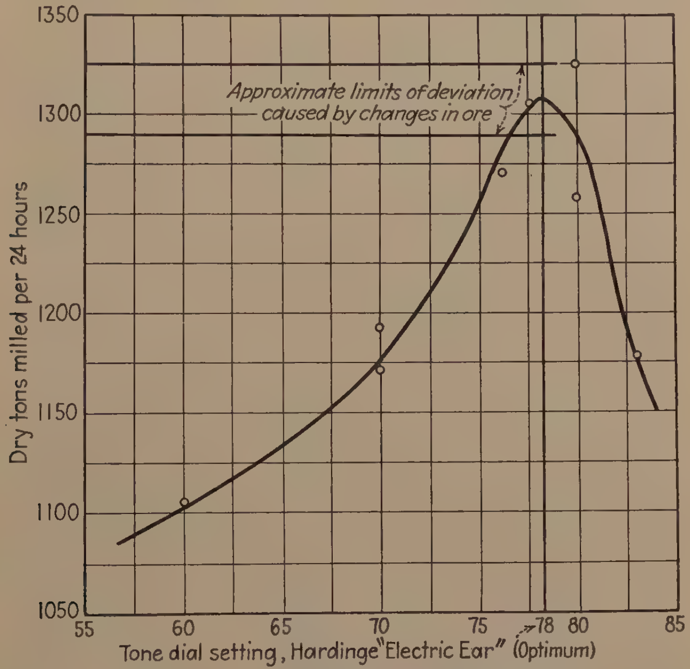


Fig. 6.—Reproduction of Graph Drawn by International Nickel Company's Staff.

Showing relation of noise level to capacity at a given fineness, by using "Electric Ear" to regulate mill-feed rate. Note radical increase in capacity near optimum noise level, an increase that takes place in a zone narrower than the human ear can detect.

The graph in Fig. 7 shows the result of tests made under various operating conditions, before and after the "Electric Ear" was installed. The average capacity at 14.5 per cent plus 65-mesh before installation of the "Electric Ear" is shown by the curve to be 1220 tons per 24 hr. The power was reported as 5.16 kw-hr. per ton. With the use of the "Electric Ear" the tonnage increased to 1304 tons and the power dropped to

4.69 kw-hr. per ton. When grinding to 12.5 per cent plus 65-mesh the average results before the "Electric Ear" was installed indicated a tonnage of 1075 tons per 24 hr. and after the "Electric Ear" was installed 1195 tons per 24 hr., an increase of 120 tons, or 11.2 per cent.

Numerous tests in other places, run under widely different circumstances, have been conducted, but the tests conducted by the International Nickel Co. are the most comprehensive and thorough on the subject so far, and show in a clear and concise manner the important factors that must be taken into account when a mill is to be controlled automatically by its own sound.

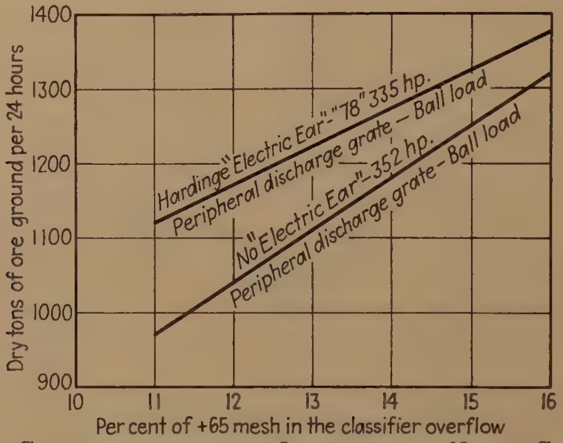


FIG. 7.—COPY OF GRAPH MADE BY INTERNATIONAL NICKEL COMPANY.

Showing comparison between operation of No. 17 ball mill with and without use of "Electric Ear." Note that at fineness 12.5 per cent plus 65 mesh the gain through the use of the "Electric Ear" was 120 tons per day, or 11.2 per cent.

## CONCLUSION

From the study made of the operation of mills by their own sound and the numerous tests conducted in one form or another, it is apparent that a mill so controlled becomes much more stable in operation and allows the operator to run it to best advantage at all times, without the necessity of keeping close watch on the variables that otherwise upset the expected results. It appears also that as the lining wears down there is not sufficient change in the noise level to require readjustment of the sound level. It also appears that if the ball load varies, the change in ball load is automatically accounted for by sound level. In other words, if the mill is not supplied with sufficient balls to take care of the wear and the ball load is reduced, this is automatically taken care of by the sound because, fewer balls being in the mill, the grinding rate is reduced and the sound level, which would otherwise be reduced, is kept the same since the "Electric Ear" in cutting the feed proportionately maintains the product constant.

It also appears that under all normal grinding conditions, whether the grinding is done wet or dry, in open or closed circuit, for granular or a very fine product, sound bears a definite relation to capacity under a given condition. It does not follow that the sound level will be the same under all conditions—it will not—but it does follow that there appears to be a sound level that will produce optimum results under any given condition, a level that must be determined by trial, in most instances at least.

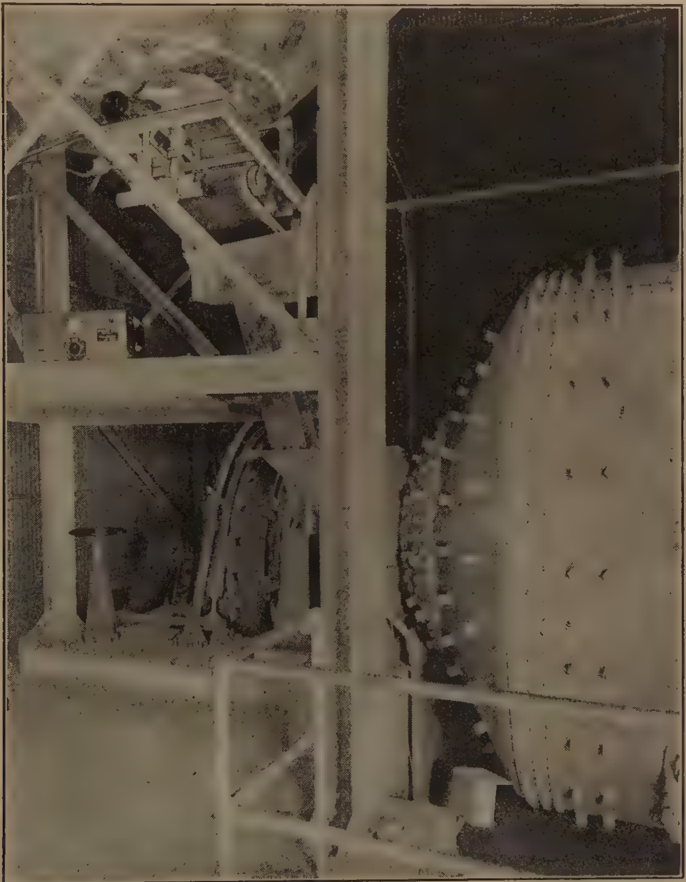


Fig. 8.—"Electric Ear" controlling feed to 10-foot conical ball mill. Constant-weight feeder attached to bottom of bin (near top of illustration) is regulated by the "Electric Ear" control cabinet on platform. Sound from mill is picked up by microphone installed near bottom of mill.

It also appears that through the elimination of the variables attendant upon manual operation, the net grinding capacity is increased, or for the same capacity a finer and more uniform product is obtainable. This statement is based on the results of a good many installations made so far on mills grinding ore, cement, coal, coke, limestone, silica sand, enamel, clay, ilmenite, chrome ore and other materials.

When the mill is maintained at full capacity and not permitted to run in an underloaded condition, it also follows that ball and liner consumption should be reduced.

It does not follow that sound is a universal means for correcting all variables, nor can it be employed in every instance. Many of the limitations have been determined already and others will appear in time, but in the so-called conventional grinding circuit the use of sound as the controlling medium has established itself as a basic factor.

### Acknowledgments

Acknowledgment with appreciation is extended to Mr. R. D. Parker, General Superintendent, and Mr. E. H. Rose, Mill Superintendent, International Nickel Co. at Copper Cliff, Ontario, for their permission to use International Nickel Co. test data in this paper.

## DISCUSSION

(*E. W. Engelmann presiding*)

T. B. Counselman,* Chicago, Ill.—Mr. Hardinge spoke of controlling the feed rate to the grinding mill by the "Electric Ear," and also of simultaneously controlling the water rate to the classifier in closed circuit with the mill. May I ask why it is necessary to control this water rate with very slight variations in the feed rate?

H. Hardinge.—It is desirable to control the water rate in order to preserve the same dilution of overflow from the classifier and maintain the same mesh of separation.

T. B. Counselman.—Can you hold the dilution of the classifier overflow constant by this control?

H. Hardinge.—Yes, and within very close limits.

W. H. Coghill,† University, Ala.—I think we owe Mr. Hardinge a great debt for conceiving and perfecting this useful device. Such a job is so expensive that it can be done only by a large and strong organization.

What is the smallest grinding medium used? The Bureau of Mines station in Alabama has been using excessively fine grinding media, only a small fraction of an inch in diameter, and a mill so loaded does not make the noise commonly expected of large media. We get only a mild swishing sound. Would the "Electric Ear" apply in such a case?

H. Hardinge.—There is no reason why it should not apply. The smallest balls in mills so far operated with the "Electric Ear" have ranged from about ½ to 1 in. average in diameter. As to the volume of sound required, we have operated wet-grinding mills in closed circuit with classifiers where the sound of the balls could not be heard above sounds near by, unless we listened close to the point at which the balls struck the shell of the mill. Sometimes even the gear of the mill makes more noise than the balls, but utilizing the additive effect of both and the variation of one we can attain proper control.

---

* The Dorr Company, Inc.

† Metallurgist, U. S. Bureau of Mines.

# First Magnetic Roasting Plant in Lake Superior Region

By E. W. Davis,[*] Member A.I.M.E.

(New York Meeting, February, 1937)

If the tonnage of merchantable iron ore remaining in the Lake Superior district is divided by the average of the annual shipments for the past 20 years, it will be found that this ore supply will be exhausted in approximately 35 years. This computed exhaustion period would be an indication of the future activities of the iron-mining industry if it were not for the fact that merchantable ore is being manufactured from low-grade ore, of which there is an almost inexhaustible supply in the Lake Superior district. It is true that at present only the simplest of these low-grade ores are being concentrated to any considerable extent, but progress is being made with the treatment of the more complex ores, and now, in addition to 20 washing plants on the Mesabi Range, three plants are equipped with jigs for the treatment of ore that cannot be concentrated simply by washing. The latest addition to the ore-treating plants of the Mesabi Range is a magnetic roasting and concentration plant at Cooley, Minn., in which ore that cannot be concentrated either by washing or by jigging is roasted to the magnetic state and concentrated on magnetic separators. This plant is beginning its third season of operation, and while it is too soon to make definite predictions, there are strong indications that this new process may make commercially possible the manufacture of high-grade, merchantable iron ore from large quantities of low-grade ore now considered worthless.

After the iron oxide contained in an ore has been converted to magnetite, almost any desired grade of concentrate can be produced, using magnetic-concentration equipment of the types now in general use for the concentration of the natural magnetites of New York, New Jersey and Pennsylvania. The conversion of hematite ($Fe_2O_3$) to magnetite ($Fe_3O_4$) is easily accomplished by heating the ore to a dull red temperature in a reducing atmosphere. The reaction is slightly endothermic, and while it requires 200 B.t.u. to heat to 900° F. one pound of hematite ore containing 45 per cent Fe, it requires only 100 B.t.u. to convert the oxide into magnetite. In the laboratory, using small quantities of ore, this conversion is very simple, but large furnaces suitable for commercial

---

Manuscript received at the office of the Institute July 15, 1936. Issued as T.P. 731, November, 1936.

[†] Superintendent, Mines Experiment Station, University of Minnesota, Minneapolis, Minn.

use are not available, and several years ago the Mines Experiment Station of the University of Minnesota undertook the development of a magnetic roasting furnace that would be specifically applicable to the treatment of the low-grade ores of the Lake Superior district.

It was desired to roast the ore at a comparatively coarse size in order to produce concentrate of as large a size as possible, therefore the investigation of shaft-type furnaces was undertaken, because this type handles coarse ore satisfactorily and possesses other advantages such as simplicity of construction, freedom from moving parts and efficiency of heat transfer. Shaft-type furnaces of several sizes and kinds were constructed and studied, and early in 1934 it appeared that the results secured warranted the construction of a larger furnace for commercial use. Accordingly, an arrangement was made with Butler Brothers of St. Paul, Minn., whereby the University of Minnesota erected a 250-ton roasting furnace at Cooley, Minn., and Butler Brothers constructed the ore-handling equipment and the magnetic-concentration plant. The roasting furnace and concentration plant were operated during the 1934 and 1935 ore-shipping seasons as an experimental unit under the direction of the staff of the Mines Experiment Station, and during this period 29,074 tons of tailings rejected from two near-by jigging plants were roasted and concentrated magnetically, resulting in the production of 15,870 tons of merchantable ore. The University's interest in this plant was then sold to Butler Brothers, who put the plant into commercial operation in the spring of 1936.

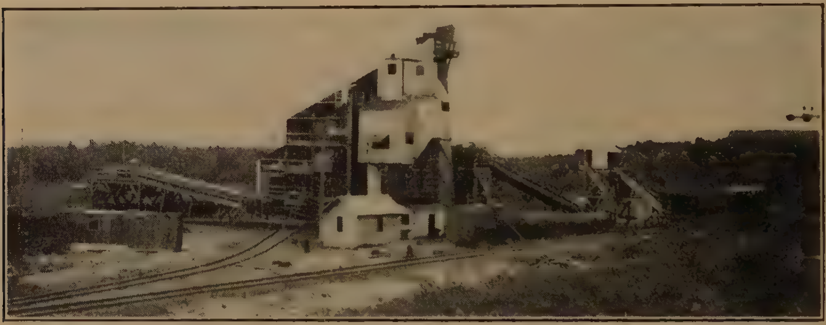


FIG. 1.—COOLEY ROASTING AND MAGNETIC CONCENTRATION PLANT.

During the two years in which the Experiment Station operated the Cooley roasting furnace, several changes were necessary in certain details of the design, primarily because of difficulties traceable to the improper movement of the ore through the shaft of the furnace. The subject of ore movement has been studied in considerable detail, but the information that has been secured is by no means complete. In the description that follows, the furnace in its final form, as it appeared at the beginning of the 1936 season, is described in detail.

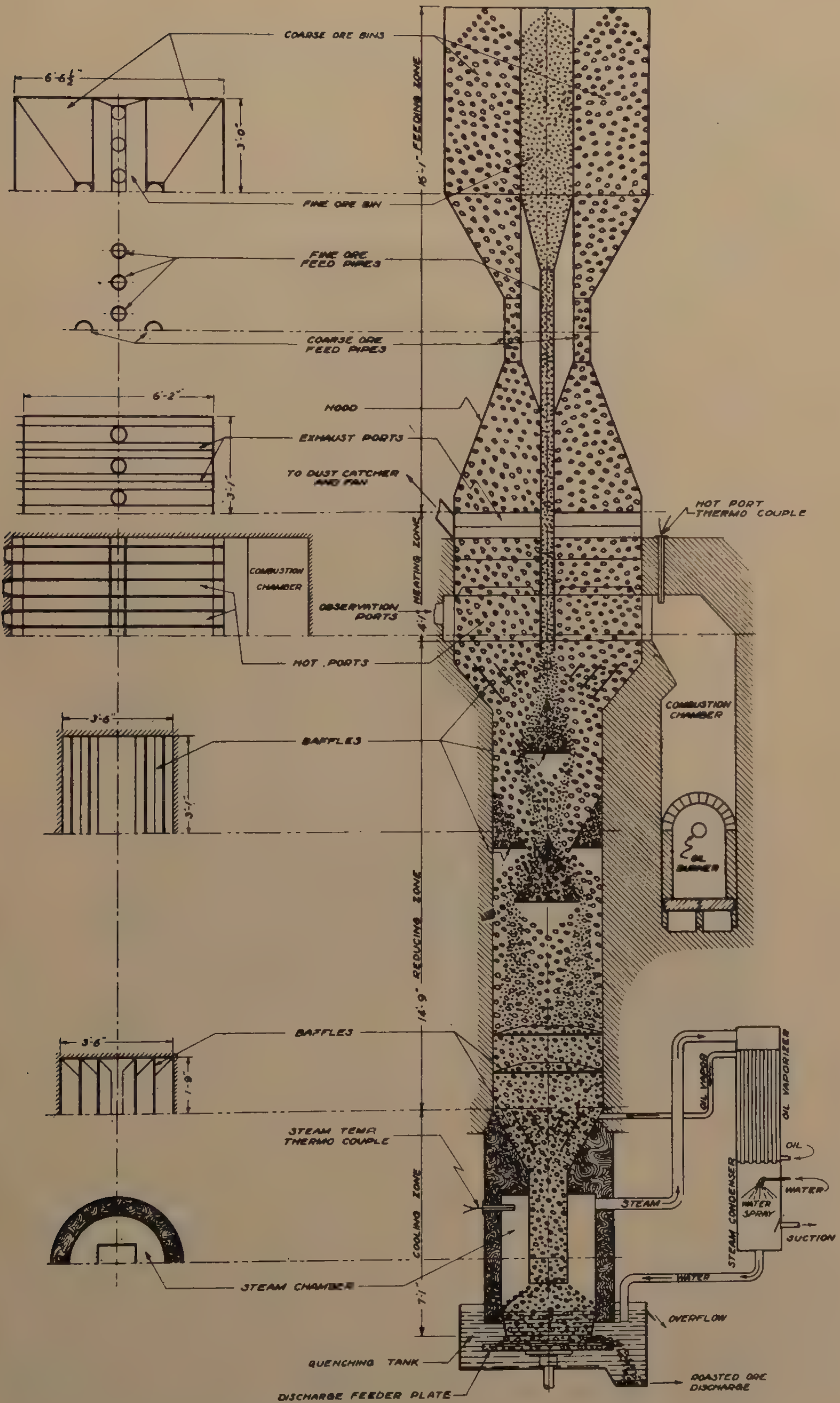


FIG. 2.—DIAGRAMMATIC DRAWING OF COOLEY ROASTING FURNACE.

## COOLEY ROASTING FURNACE

The Cooley furnace in its present form is shown in diagrammatic cross section in Fig. 2. The ore to be roasted is crushed to $-\frac{3}{4}$ in. and then screened at 4 mesh, the oversize going into the two coarse-ore bins and the undersize into the fine-ore bin. The three bins together have a capacity of 10 tons of ore, in the proportion of 8 tons of coarse ore and 2 tons of fine ore. During the operation of the furnace, these bins are not allowed to become entirely empty, thus keeping the entire shaft of the furnace filled with ore at all times. The ore is discharged from the bottom of the furnace by a rotary feeder, and the rate at which the ore is drawn from the bins at the top of the furnace is regulated by the rate at which the feeder is operated.

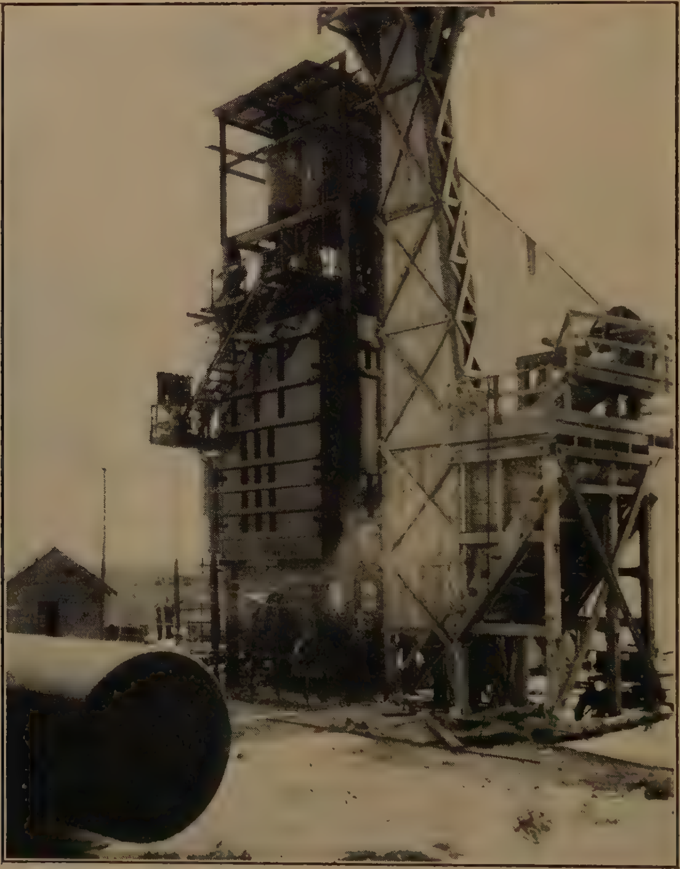


FIG. 3.—ROASTING FURNACE DURING CONSTRUCTION.

From the coarse-ore bins, the ore passes through pipes of restricted cross section, the purpose of which will be explained later. It then passes into the hood, the purpose of which is to spread the ore out to the full size of the furnace shaft. The angle of the sides of the hood to the horizontal is 60°, which is greater than the angle of repose of the ore, and since the ore is pressed against the surface of the hood at all times, no rolling of the individual particles is possible. The ore next enters the heating chamber of the furnace. In its descent through this chamber, it passes the exhaust ports and then the hot ports. The exhaust ports are tubular members, open at the bottom and extending completely across the heating chamber. The hot ports have the cross section shown in Fig. 4. Hot gases, the products of combustion from the oil burners in the combustion chamber, are drawn into the hot ports and pass into the ore through the openings under the roof. The hot gases pass upward through the ore and escape through the exhaust ports into the dust catcher and fan. The resistance in the system is such that for the quantity of hot gases required, a suction at the fan of 10 in. of water is necessary. The contraction in area at the bottom of the coarse-ore bins referred to above is necessary in order to prevent excessive leakage of air downward through the ore bins and hood and into the exhaust ports. With the construction shown, the leakage amounts to only about 5 per cent.

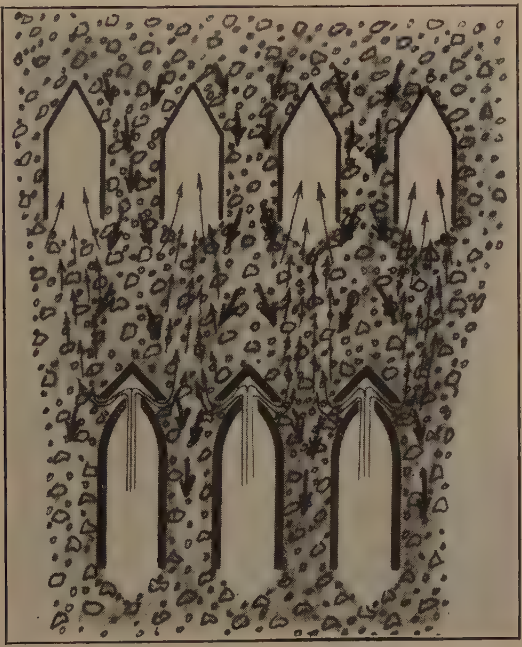


FIG. 4.—HEATING ZONE SHOWING HOT PORTS AND EXHAUST PORTS AND DIRECTIONS OF ORE AND GAS FLOW.

Large arrows show direction of ore movement downward; small arrows show direction of gas flow upward.

After passing the hot ports, the coarse ore passes into the reducing chamber, where it meets the reducing gases. The fine ore, which has been shunted around the heating zone, is allowed to mix with the coarse ore at this point. Had the fine ore not been removed from the coarse ore before it passed through the heating zone, the power required by the fan would have been materially increased and the dust losses would have been excessive. On account of the fact that the fine ore is not heated directly, it is necessary to make the coarse ore hotter than would otherwise be necessary, in order that it may give up part of its heat to the fine ore and still be sufficiently hot for rapid reduction.

The temperature to which the coarse ore must be heated for the resulting mixture of coarse and fine ore to have the required temperature may be computed when the proportion of coarse to fine ore is known and the resulting temperature is determined. In the Cooley furnace, the desired temperature of the mixture is about 1100° F., and since the ratio of coarse ore to fine ore is about 5:1, it is necessary to heat the coarse ore to a temperature of about 1270° F. If the ratio is 4:1, it will be necessary to heat the coarse ore to 1310° F.; and if the ratio is 3:1, a temperature of 1370° F. It is doubtful whether this type of furnace can be operated satisfactorily with a ratio of coarse to fine ore of much less than 3:1, because of the difficulty of heating the coarse ore to the high temperature required. This limitation in temperature is not due to the melting or softening of the coarse ore, since there is little danger of this occurring below a temperature of 2000° F., but is due to the fact that the hot port castings are constructed of high-temperature alloy steel, which for long life should not be operated continuously at a temperature above 1800° F. This limits the temperature of the products of combustion entering the hot ports, and since the rate of heat transfer between gas and ore is proportional to the difference in temperature, the rate of heat transfer decreases rapidly as the temperature of the ore approaches the temperature of the products of combustion. If it is necessary to heat the coarse ore to a higher temperature, the time of contact between the hot gases and the ore must be increased, which means either a slower feed rate and, therefore, a reduced capacity, or a longer path of travel of the gases through the ore, which means a material increase in the power required by the fan.

The minimum temperature of the gases leaving the exhaust ports is determined by the amount of water in the ore and in the products of combustion that the gases must carry away as vapor. Since it is not possible to determine definitely the maximum amount of water that the ore may carry, because of rain, snow, etc., the exhaust ports are placed 18 in. above the hot ports in the Cooley furnace in order to maintain a minimum temperature of the exhaust gases of about 200° F. At this temperature, the carrying power of the gas for water vapor is so large that even abnormal quantities of moisture are handled without difficulty. The fine ore that by-passes the heating zone passes over and around the hot ports and receives some heat from them by direct contact, but since gases cannot pass upward through the fine ore, the amount of heat that it absorbs is little more than sufficient to vaporize the moisture it contains.

The combustion chamber, which supplies the hot gases to the hot ports, is designed for the combustion of fuel oil. It may also be used with either natural or artificial gas, but if stokers or pulverized-coal burners are used, radical changes in design will be necessary. In the Cooley furnace, an oil burner is placed at each end of the combustion chamber, and these are so operated that no flame enters the hot port castings. This is an important consideration, since flame in these castings may cause overheating and rapid deterioration of the alloy steel. Thermocouples are placed in the entrance to the hot ports, and the oil burners are so operated that these couples register a temperature of approximately 1800° F. at all times. Automatic temperature controls could be installed, if desired, but no attempt was made to make the Cooley furnace automatic, since it was largely experimental.

Uniform heating of the coarse ore is essential for satisfactory operation, and this can be accomplished only by having a uniform flow of gas upward through the entire cross section of the heating zone and a uniform movement of the ore downward through the hot gases. No difficulty was encountered in securing a uniform gas flow, but considerable study was necessary in order to secure uniform movement of the ore. Whether or not the movement of the ore at this point is uniform depends entirely upon the movement of the ore below the heating zone. For structural as well as metallurgical reasons, it was necessary to reduce the cross section of the furnace below the heating zone, and this reduction in area caused the ore movement to be nonuniform. This reduction in cross section is desirable in order to increase the velocity of flow of the reducing gases upward through the ore and also to simplify the problem of uniformly mixing the fine ore with the coarse ore. A uniform mixture of the ore at this point is desirable in order to produce an ore column through which the reducing gases may pass without channeling. The method of baffling used to secure uniform motion of the coarse ore through the heating zone is shown in the drawing, and while this method of baffling does not produce absolutely uniform motion, tests indicate that it is sufficiently uniform for all practical purposes. Fig. 2 shows these baffles in their present form, but several changes in the shapes and locations of these baffles were made before satisfactory operation was secured.

The mixing of the fine ore with the coarse ore was found to be a difficult undertaking. It was necessary to arrange baffles not only to mix the coarse and fine ore but also to regulate the amount of fine ore that flows into the reduction chamber from the fine-ore bin. The small, round baffle in the middle of the fine-ore compartment just below the hot port castings is used to control the rate of flow of the fine ore, and by raising or lowering this baffle a few inches the amount of fine ore passing into the reducing chamber can be controlled within reasonable limits. The various baffles in the reducing chamber are designed to mix the coarse and fine ore and, at the same time, give the reducing gases access to all of the ore particles. The open spaces below these baffles equalize the gas pressure and produce the desired directions of flow, since the gases tended to flow from one open space to the next above. Near the bottom of the reducing chamber, the cross section of the furnace is again reduced in order to discharge the ore through a small central opening. From full-size model tests, the arrangement of baffles in the lower part of the reduction chamber was determined and proved to be entirely satisfactory in the operation of the furnace, although the baffles in the upper section of the furnace were changed several times.

The gas used for reducing the ore enters the furnace near the bottom of the reducing chamber at the point shown in the drawing. The reducing gas now in use is formed by vaporizing fuel oil in a vaporizer heated by steam from the steam chamber. The vaporizer is similar to a fire tube boiler, the high-temperature steam passing downward through 2-in. pipes which are surrounded by the oil to be vaporized. The temperature of the steam is about 1000° F., and the boiling point of the oil used is about 600° F. In the vaporizer, the oil is not only vaporized but the vapor is also superheated to a temperature of about 900° F. The oil, pumped into the vaporizer at a rate that produces the required flow of reducing gas, assumes a level in the vaporizer depending upon the amount and temperature of the steam that is being produced in the steam chamber. This method for the production of a reducing agent is entirely satisfactory, although the reducing agent itself can be materially improved by converting the hydrocarbons into hydrogen and carbon monoxide. No attempt is made to crack the oil in the vaporizer, but upon entering the reducing chamber in contact with the iron oxide, reactions occurred that produce principally methane, carbon, carbon monoxide and hydrogen, the two latter being the active reducing agents. The carbon is discharged from the furnace with the ore and is lost, and the methane passes upward through the reducing chamber and burns in and around the hot ports. This causes considerable trouble at times, because this combustible gas occasionally channels up through the ore and burns at some particular point. This tends to cause local overheating of the ports, which, if permitted to continue, will produce warping and rapid deterioration of the alloy steel. In order to eliminate this difficulty, it is necessary at times to withdraw part of the unconsumed gases from the furnace at the top of the reduction chamber and burn them in the combustion chamber. If a more desirable reducing agent were available containing no methane or other hydrocarbons, the flow of this gas could be so adjusted that practically all of the combustible would be consumed in contact with the ore before the gases reached the hot ports. This would not only be a more efficient method for reducing the ore but would eliminate some of the difficulties encountered in the operation of the furnace.

After descending through the reducing chamber, the ore enters the cooling chamber through a pipe considerably smaller in cross section than either the reducing chamber or the cooling chamber. This reduction in cross section is desirable in order to prevent the flow of reducing gases into the cooling chamber and in order to control the flow of steam from the cooling chamber into the reducing chamber. The cooling chamber is surrounded by a tank of water that is maintained at a constant level by a float valve. The water in this tank not only seals the bottom of the furnace and prevents the flow of gases into the air, but also provides the means for cooling the ore. The rotary feeder plate, as shown on the drawing, is below the level of the water, and as the feeder plate rotates, the hot ore from the reducing chamber slowly moves downward into the water, producing steam, which escapes through the pipe shown in the drawing, and warm water, which is removed from the tank with the ore. The steam is formed where the hot ore meets the water, which is at a level below the surface of the ore in the steam chamber. The steam formed must, therefore, pass upward through the ore in order to escape from the chamber. This contact between the steam and the hot ore superheats the steam to a temperature that is approximately the same as the temperature of the ore. A thermocouple in the steam outlet from the cooling chamber is a direct indication of the temperature of the ore being discharged and is used as one of the major operating controls.

In order to prevent reducing gases from passing downward into the steam chamber, it is necessary to keep the steam pressure equal to or greater than the pressure of the gases in the reducing chamber. The presence of a limited amount of steam in the reducing chamber is desirable; it tends to prevent overroasting and also reacts with the oil vapor, to some extent, to produce hydrogen and carbon monoxide. Oil vapor is a concentrated reducing gas, therefore the quantity required is small and the pressure in the reducing chamber seldom exceeds ⅛ in. of water. The best operating conditions are obtained by maintaining a steam pressure of about ¼ in. of water. This pressure prevents the flow of reducing gases downward and provides the desired amount of steam in the reducing chamber.

The method used for controlling the pressure of the steam in the cooling chamber is very simple. As previously stated, the superheated steam, after leaving the cooling chamber, passes through the oil vaporizer. From that vaporizer it enters the condenser, where it meets several water sprays, which condense all of the steam, leaving only the noncondensable gases, consisting of the air that was in solution in the water and the hydrogen that was formed by chemical reactions in the cooling chamber. The quantity of these noncondensable gases is small, and they are pumped from the condenser with a small suction pump. By controlling the suction on this pump, the pressure of the steam in the cooling chamber can be adjusted as desired. The noncondensable gases are at times an explosive mixture and therefore are passed through an explosion trap before they enter the combustion chamber. In the Cooley furnace, no use is made of the hot steam except for vaporizing the oil for reduction purposes, but this steam may be used for any purpose desired, the only requirement being that control means must be available so that the pressure in the reduction chamber may be regulated as desired. If the steam is used for some useful purpose, a material saving in heat units can be secured, since the steam contains about two-thirds of the heat absorbed by the ore in the heating zone. In the Cooley furnace, approximately 200 lb. of steam at a temperature of 1000° F. is produced per ton of ore fed to the furnace. It is at a pressure of about ¼ in. of water and contains considerable dust, part of which is as coarse as 20 mesh. This dust is all in the form of magnetite and is returned to the quenching tank with the water from the condenser. If the steam is to be used for other purposes, the dust must be removed, the degree of cleanliness required depending upon the use to which the steam is put. Any degree of cleanliness desired can be secured by the use of Cottrell precipitators.

## Alloy-steel Ports and Baffles

The hot ports and all of the baffles in the furnace are made of an alloy of iron, nickel and chromium, the exact proportion of these three elements in the alloy depending upon the service required. Before the castings could be made, it was necessary to determine the load that each member would be required to carry. In order to determine these loads, a full-size wooden model of the furnace was constructed, filled with ore, and the deflection of each member measured. The ore was then removed from the furnace, and each member was loaded with iron weights in order to produce the same deflection as had been observed when the model was filled with ore. By this method it was possible to determine approximately the load to be supported by each alloy member, and with this information and knowing the temperature and gas analysis at each point in the furnace, it was possible to design the various members.

High-temperature alloy steel has certain characteristics that must be considered when used in a furnace of this type. Expansion is a serious consideration, since some of the castings under operating conditions expanded 1½ in. in length and contracted again, upon cooling, to approximately their original size. It is necessary, therefore, to make ample provision for expansion, because if this is not done the castings will warp and buckle out of shape. This is illustrated by the photograph in Fig. 5, which show some of the alloy steel members that were not free to expand. It is a simple matter to allow ample expansion space in the original design, but ore dust continually works into these expansion spaces and fills them to such an extent that after the furnace is heated and cooled a few times, the castings can no longer expand freely. This difficulty may be avoided by proper design, but it was the only cause of failure of any of the alloy members in the Cooley furnace. The castings showed no sign of overheating or overloading at the end of two seasons of operation, although several of them were deformed by lack of expansion space. They were designed to retain their shape for 20,000 hr. of continuous operation, which would be about four operating seasons, and from the information that has been obtained, it is certain that the castings will last at least three seasons and, in all probability, most of them will be good for a considerably longer period of time.

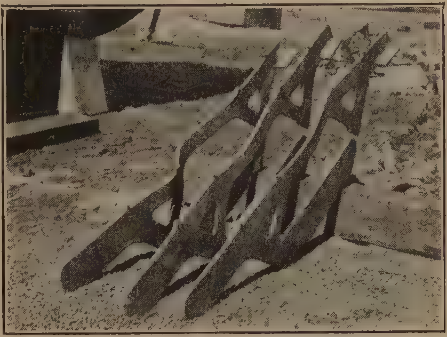


Fig. 5.—Alloy-steel castings that failed because of lack of expansion space.

## Operation of the Cooley Furnace

Under normal conditions, the operation of the furnace is quite simple. Thermocouples placed in the entrance to the hot port castings indicate the temperature of the gases from the combustion chamber, and this temperature is maintained at 1800° F. at all times by means of the controls on the oil burners in the combustion chamber. A thermocouple in the cooling chamber indicates the temperature of the steam being produced, which is approximately the temperature of the ore being discharged from the reducing chamber, and it has been found that this temperature should be maintained at approximately 1050° F. in order to produce properly roasted ore. This temperature is maintained by controlling the speed of the rotary feeder at the bottom of the furnace. If the temperature drops below 1050° F., the feeder is slowed down slightly, and if the temperature increases above 1050° F., the speed of the feeder is slightly increased. The chief duty of the operator is to maintain the temperature at the entrance to the hot ports at 1800° F. and to operate the feeder at the proper rate of speed to maintain a steam temperature of 1050° F. A pyrometer records the important temperatures throughout the furnace, and the number of revolutions per shift of the feeder indicates the tonnage of ore that the operator has been able to roast. Occasional readings were made of the oil and gas pressures at various points in the furnace during the test periods, in order to analyze more closely the operating conditions. The chief operating difficulties are due to changes in the moisture in the ore. As long as the moisture remains fairly constant, the furnace operates practically without attention, but rapid changes in moisture throw the furnace out of balance to such an extent that constant attention is required for several hours in order to again secure proper operating conditions. The furnace is operated by one man, with the assistance of a part-time helper whose principal duty it is to look after the mechanical equipment. The skill required to operate the furnace is not beyond the capabilities of an intelligent workman. At the Cooley plant, the furnace operator also acts as the shift boss.

TABLE 1.—*Furnace Operating Records, Month of September,* 1935

| | |
|---|---|
| Number of days operating | 30 |
| Operating hours | 692 |
| Lost time, per cent | 3.89 |
| Tons of feed | 5,802 |
| Total gallons of oil | 55,182 |
| Number men employed for shift | 1.3 |
| Electric power consumption, kw-hr | 19,050 |
| Gallons oil per ton of feed | 9.5 |
| Electric power per ton of feed, kw-hr | 3.3 |
| Cost per ton of feed: | |
| Oil | $0.555 |
| Power | 0.050 |
| Labor | 0.072 |
| Total | $0.677 |

Table 1 shows the principal operating data for the month of September, 1935, and also the major items of operating expense per ton of furnace feed. These figures show that the fuel cost is 81 per cent of the direct operating expense.

Table 2 shows the plant operating data for three days during the month of September when the moisture in the ore was high, normal and low, respectively. These figures show the effect of moisture in the feed on the operation of the plant; that is, the fuel consumption per ton increases and the capacity of the furnace decreases as the ore becomes wetter. This change, however, has practically no effect on the metallurgical results secured in the magnetic concentration plant, the grade of concentrate, the percentage weight recovery, and the percentage iron recovery remaining practically constant. On Sept. 22, when the ore was exceptionally dry, containing only 6.2 per cent moisture, the temperature of the steam was 1087° F., indicating that the feed rate could have been increased above 9 tons per hour. This tendency to underfeed the furnace when the ore is dry is quite usual, because it is difficult to tell by the appearance of the ore that it has decreased 1 or 2 per cent in moisture and because it is hard to convince the operators that this slight change has such a marked effect upon the operation of the furnace.

The temperature of the gases from the combustion chamber entering the hot ports is dependent only upon the amount of oil being burned and the amount of air being drawn through the combustion chamber by the fan. Since the oil burners always consume an amount of oil dependent upon the valve setting, and since the fan is operated at a constant speed, the only reason for a change in the temperature of the combustion gases is a change in the resistance to the flow of the gases through the heating zone, and a change in this resistance is caused only by a change in the screen analysis of the coarse ore. The crude ore is screened normally at ¼ in. on a vibrating screen, but when it is exceptionally wet it is necessary to use a ⅜-in. screen. Even with the use of this coarser screen, the oversize contains considerably more fine ore than when drier material is screened at ¼ in. For this reason, when wet ore is encountered, necessarily more fine material passes through the heating zone with the coarse ore, thus increasing the resistance to the flow of the gases and decreasing the amount of oil that may be burned in the combustion chamber, and this occurs at a time when additional heat is necessary for the evaporation of the additional water. This statement may be justified from the furnace records, which show that the amount of oil burned per hour is actually less when the ore is wet than when it is dry.

TABLE 2.—*Effect of Moisture in Ore on Plant Operation*

| | High Moisture | Normal | Low Moisture |
|---|---|---|---|
| Date | Sept. 24 | Sept. 15 | Sept. 22 |
| Hours of operation | 23.3 | 24 | 22 |
| Tons feed per hour | 7.4 | 8.5 | 9.0 |
| Ratio, coarse to fine ore | 7:1 | 7:1 | 7:4 |
| Furnace feed: | | | |
| Per cent Fe | 50.30 | 49.07 | 49.10 |
| Per cent moisture | 8.6 | 7.4 | 6.2 |
| Gallons oil per ton: | | | |
| Combustion | 6.79 | 6.18 | 5.85 |
| Reduction | 3.55 | 3.30 | 3.15 |
| Temperature at entrance to hot ports, deg. F | 1818 | 1820 | 1816 |
| Temperature at exit from exhaust ports, deg. F | 220 | 202 | 204 |
| Temperature of steam chamber, deg. F | 1038 | 1020 | 1087 |
| Furnace product: | | | |
| Per cent Fe | 53.55 | 52.20 | 52.26 |
| Per cent C | 0.64 | 0.50 | 0.55 |
| Roasting efficiency | 90.0 | 89.2 | 91.1 |
| Magnetic concentrate: | | | |
| Per cent Fe | 62.12 | 62.18 | 62.02 |
| Per cent weight recovery | 71.8 | 70.1 | 70.6 |
| Per cent Fe recovery | 88.7 | 88.6 | 89.0 |
| Tons per hour | 5.31 | 5.96 | 6.47 |

These facts are shown by the curves in Fig. 6, which show the changes in capacity and fuel consumption as the moisture changes in the ore.

As the ore becomes wetter, owing to rain or other causes, the first noticeable effect on the operation of the furnace is an increase in the temperature of the hot gases from the combustion chamber. This makes necessary an immediate reduction in the amount of oil being burned in order to reduce the temperature to normal. The next effect is a decrease in the temperature of the steam, indicating that the ore in the reduction chamber is cooler. To counteract this, it is necessary to reduce the feed rate until the temperature of the steam again reaches normal. If this is not done, the quality of the roast decreases rapidly. The effect on the quality of the roast of a change in the temperature of the ore as indicated by the temperature of the steam is shown by the curves in Fig. 7. These curves indicate that for a roasting efficiency of 90 per cent, the temperature of the steam should be about 1040° F. Roasting efficiency is defined as the percentage of iron as magnetite divided by the percentage of total iron in the furnace product. As the steam temperature decreases, the efficiency falls off rapidly, and as it increases, the efficiency increases slowly. A thermostatic control that would automatically change the speed of the feeder in order to maintain a constant steam temperature

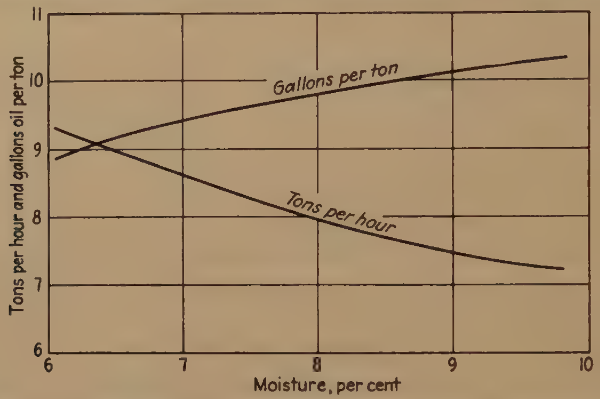


Fig. 6.—Effect of moisture in ore on furnace capacity and oil consumption.

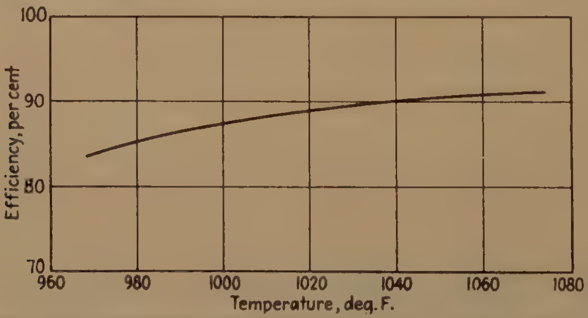


Fig. 7.—Relation between steam temperature and roasting efficiency.

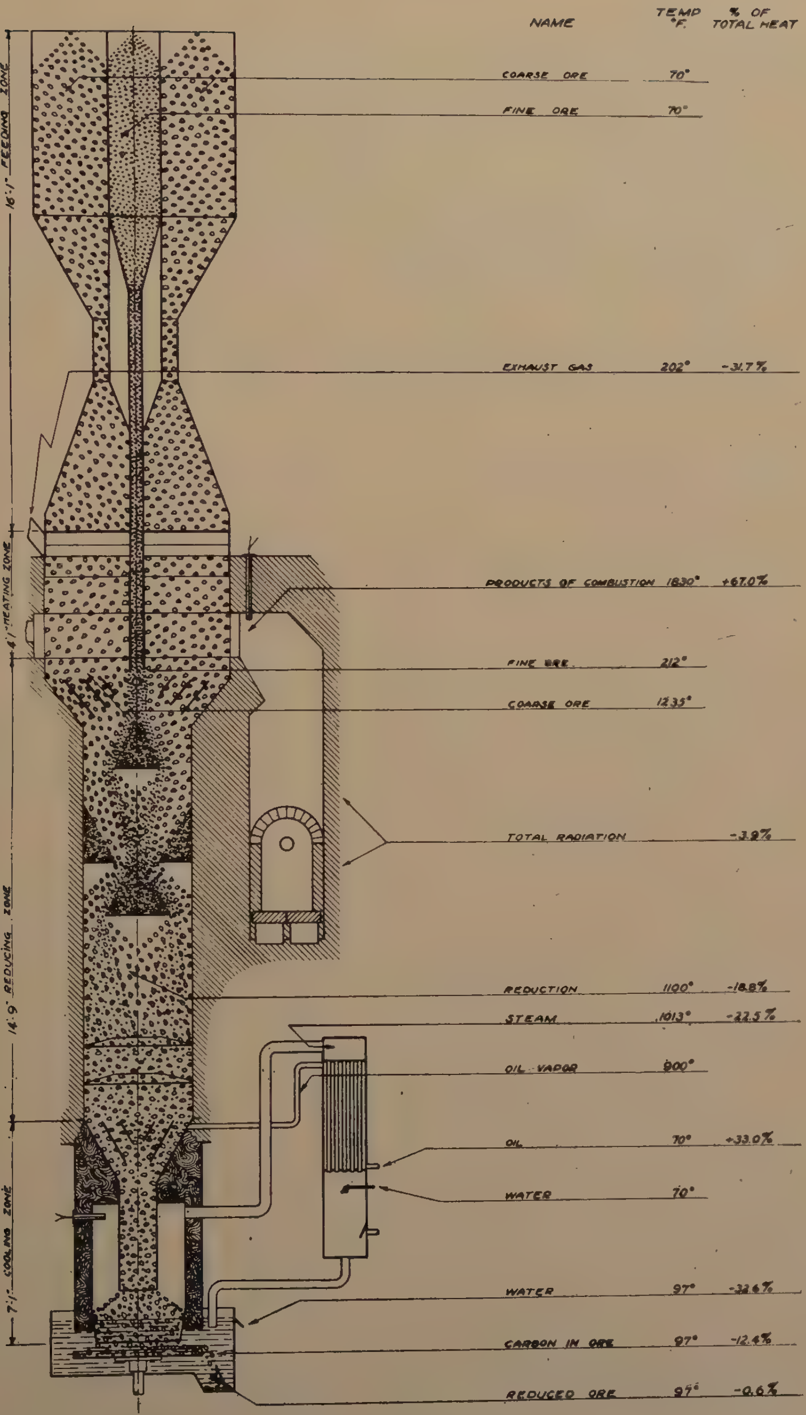


FIG. 8.—DIAGRAMMATIC DRAWING OF COOLEY FURNACE SHOWING TEMPERATURE AND HEAT DISTRIBUTION.

could be installed, but frequently the furnace operates throughout an entire shift with no adjustment to the feed rate, and the cost of automatic controls could not be justified on the single unit of the Cooley furnace.

From the above information, it is evident that most of the operating difficulties and irregularities are due to changes in the moisture of the ore. If the ore could be dried before screening and before feeding to the furnace, most of the operating difficulties would disappear, the fuel consumption per ton would be materially reduced, and the capacity of the furnace would be materially increased. Efforts are being made at the present time to determine the effect of drying the ore on the operation of the furnace, using for the purpose a drier heated either with steam from the furnace or with auxiliary fuel.

## Heat Distribution

The diagram in Fig. 8 shows the temperatures at different points in the furnace and the percentage of the total heat added that is removed from the furnace at various points under normal operating conditions. The total heat required per ton of ore is 1,402,570 B.t.u., 67 per cent of which enters the furnace at the oil burners in the combustion chamber, and 33 per cent of which enters the reducing chamber as oil vapor. Of this total heat, 31.7 per cent is lost in the stack gases, 32.6 per cent escapes as warm water from the quenching tank, 12.4 per cent is lost as carbon with the ore, and only 18.8 per cent is used for the useful work of reduction. A study of these various heat losses indicates the possibility of materially reducing the fuel consumed per ton of ore and increasing the fuel consumed per hour.

The stack gases are discharged at a temperature of 202° F. Reducing the temperature of these gases to 150° F., at which temperature they are saturated with water vapor, would save only 8 per cent of this heat loss. An analysis of the gas, however, indicates that the heat required to vaporize the water contained in the gases is 85 per cent of the total heat they contain. Part of this water is the result of reactions in the reducing and combustion chambers, but much of it enters the furnace with the ore. The ore ordinarily contains 7.5 per cent moisture and 6 per cent water of crystallization, making a total of 292 lb. of water per ton of ore. Of the total heat in the exhaust gases, amounting to 441,520 B.t.u. per ton of ore, 323,000 B.t.u., or 73.2 per cent, represent the latent heat of vaporization of the 292 lb. of water in the ore. This amount of heat may be produced by the combustion of 2.2 gal. of oil, and if this water were removed from the ore before it entered the furnace, the fuel consumption would be reduced by nearly 25 per cent. The moisture in the ore can easily be removed in a standard ore drier, but the water of crystallization can be moved only at a temperature of 1000° F. or above, which could not be secured in an ore drier without considerable difficulty and expense.

However, the fuel required for the operation of an ore drier would be approximately the same as the fuel saved by using dry ore in the furnace, and, therefore, the only saving made by drying the ore would be due to the increase in capacity that would be secured. If waste heat is used, however, the saving in fuel consumption would be as indicated.

As shown in the diagram, 22.5 per cent of the total heat required by the furnace is discharged from the cooling chamber as superheated steam. This amounts to 317,000 B.t.u. per ton of ore. More than sufficient hot air may be produced from the steam in a properly designed heat interchanger to completely dry the ore and, if desired, the excess may be used in the combustion chamber to replace the cold air with which the oil is burned. The use of the heat in the steam for these purposes would make a material saving in the fuel required for the operation of the furnace.

The use of oil vapor for the reducing agent results in the deposition of carbon on the particles of ore. This carbon is discharged from the furnace with the roasted ore and is a distinct loss, amounting to 11.92 per cent of the total heat required by the furnace, or 167,220 B.t.u. per ton of ore. This is the equivalent of 1.1 gal. of fuel oil. This loss may be eliminated by the use of a gas that does not crack and deposit carbon under the conditions encountered in the reducing chamber.

By taking advantage of the possible savings in fuel that have been discussed, it is estimated that it may be possible to roast ore containing 7.5 per cent moisture and 6 per cent water of crystallization with the consumption of approximately one million B.t.u. per ton of feed. This quantity of heat may be secured by the combustion of 80 lb. of coal, 7 gal. of fuel oil, or 1000 cu. ft. of natural gas.

## Conclusion

It is not suggested that this process in its present state of development can be used indiscriminately for the concentration of all low-grade iron ore. Roasting costs are still much too high for this process to be used generally. At Cooley, the single unit plant can be operated at a small profit only because the ore being treated is waste material from existing concentration operations, washed, crushed to size, and with no mining cost charged against it. Further improvements, some of which have been suggested, may make possible the utilization of other lean ores that are advantageously located and in proper physical condition, but before a reasonable profit can be made by treating ore that has not already been mined and properly prepared for this process, mining costs must be reduced materially. Two of the largest items of expense are royalties and taxes, and if high-grade ore is to be manufactured extensively from the lean ores of the Lake Superior district by magnetic roasting, or any other process, the fee owners must be willing to accept smaller royalties and the present tax law must be modified and clarified.

## DISCUSSION

(*Charles E. Locke presiding*)

C. E. Locke,* Cambridge, Mass.—What was the analysis of the nonmagnetic residue?

J. J. Craig,† Minneapolis, Minn.—It was 3 to 4 per cent magnetic iron or 18 to 20 per cent total iron.

F. A. Jordan, Youngstown, Ohio.—What is the future program for this plant?

J. J. Craig.—It will undoubtedly expand.

R. E. Crockett,‡ Dover, N. J.—What is the efficiency of magnetic roasting?

J. J. Craig.—In this work 90 per cent of the iron was converted into a magnetic oxide, and this was shown to be very good work in comparison with a plant in Manchuria, which made only 75 per cent conversion.

O. Lee,§ Birmingham, Ala.—Wedge roasters were formerly used. Why was the change made?

J. J. Craig.—A simpler design was desired, and lower-cost furnace without moving parts. For that reason a shaft furnace of special design was installed.

J. W. Neill,|| Pasadena, Calif. (written discussion).—Mr. Davis' paper calls to mind some data concerning a plant erected in Manchuria some 10 years ago for the same purpose. The following data were obtained from a publication by the leading engineering society of Japan (name unknown to me) in the Japanese language. This publication was submitted for my inspection while I was Chief Engineer for the Matsukata interests, in charge of the developments at the iron deposits in northern Japan. The text was largely beyond the powers of my nontechnical interpreter, but the drawings, analyses, and some details were given in English, and from these I was able to gather the data given here.

The plant was erected at the Anshan mines of the South Manchuria Railway Co., in South Manchuria, and it replaced a plant for wet crushing and gravity concentration, which had given very poor recovery percentages. The ores of the Anshan mine are exceedingly hard, an intimate mixture of hematite and quartz, as shown by photomicrographs given in the paper, and require very fine grinding to effect any reasonable separation of the minerals, thereby causing heavy costs for grinding and also heavy losses.

The roasting plant of the new installation consisted of a battery of furnaces (kilns), each 7 meters long, 2 meters wide and 10 meters high, each of a given capacity of 200 to 300 tons per day. They were heated by gas at a point 3 meters above the bottom; producer gases being used, derived from producers of what appeared ordinary construction. The furnaces (kilns) were not closed at the bottom, but the charge was supported by a set of grate bars (apparently square), which could be rotated to dis-

---

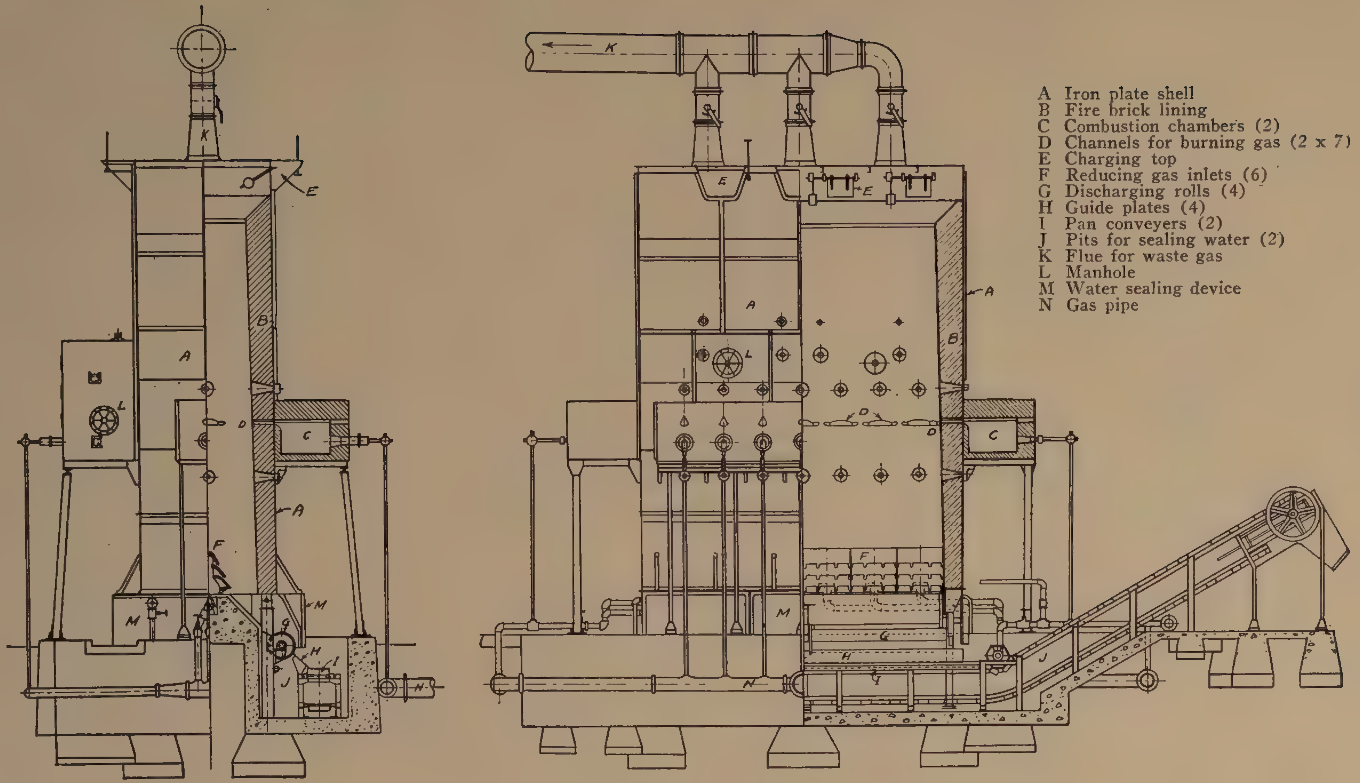
* Professor of Mining and Ore Dressing, Massachusetts Institute of Technology.

† Superintendent, Magnetic Plant, Mines Experiment Station, University of Minnesota.

‡ Superintendent, Alan Wood Steel Co.

§ Metallurgist, Republic Steel Corporation.

|| Mining Engineer, Geologist, Metallurgist.



| | |
|---|---|
| A | Iron plate shell |
| B | Fire brick lining |
| C | Combustion chambers (2) |
| D | Channels for burning gas (2 x 7) |
| E | Charging top |
| F | Reducing gas inlets (6) |
| G | Discharging rolls (4) |
| H | Guide plates (4) |
| I | Pan conveyers (2) |
| J | Pits for sealing water (2) |
| K | Flue for waste gas |
| L | Manhole |
| M | Water sealing device |
| N | Gas pipe |

Fig. 9.—Magnetic roasting furnace at Anzan.

charge the roasted ore into cars placed in a closed compartment below. There was no apparent effort for exclusion of air, and the material as discharged must have been still hot. There were appliances for regulation of the gas supply and/or air at the firing ports there, but I do not know how they were operated.

| Material | $SiO_2$ | Fe | $Al_2O_3$ | CaO | MgO | S | P |
|---|---|---|---|---|---|---|---|
| Ore | 43.74 | 38.57 | 0.40 | 0.01 | 0.15 | 0.01 | 0.026 |
| Concentrate | 13.94 | 60.80 | 0.74 | 0.4 | 0.08 | 0.03 | 0.029 |
| Sinter | 14.53 | 61.40 | 0.70 | 0.4 | 0.07 | | |

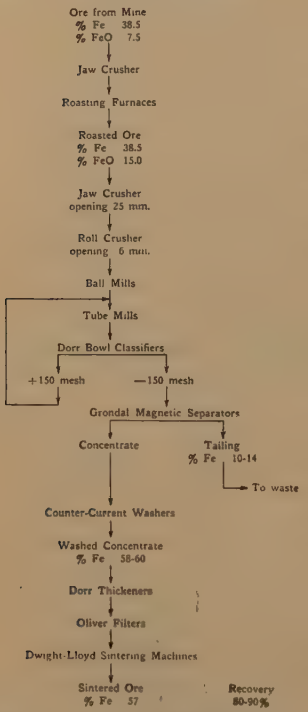


Fig. 10.—Flowsheet at Anzan.

The feed was crushed by jaw crushers to about 2 in. and no separation of coarse and fines was provided, everything going into the furnace by tramcar. The roasted ore was trammed to the old milling plant and there wet-crushed to 150-mesh (stated). It was found that the roasted ore was very much easier to crush, and the saving on this item alone nearly paid the cost of roasting. The crushed pulp was magnetically treated on Grondahl separators, the concentrates recovered by Oliver filters, then mixed with fine coal and sintered on Dwight-Lloyd machines, the sinter going to the blast furnaces. Analyses were given as shown in the table above.

The plant was calculated to handle 2600 tons per day and to produce 1200 tons of sinter. Its construction cost was placed at ten million Yen ($5,000,000) but the costs of the operation were not stated. It was merely stated that it was expected to reduce the "losses" by one million Yen per year.

As the method was not applicable to the ores of the deposit on which I was working—an ancient ocean beach containing magnetic sands—I did not visit the plant, but a friend told me that the row of Grondahl separators was so long "it vanished in the distance."

E. W. Davis.—A description of the plant about which Mr. Neill writes was published by the University of Minnesota, and is, so far as I know, the only description in English.[1]

When the paper was written the Showa Steel Works was producing 660,000 tons of sintered ore annually, with 18 furnaces, and expected to increase capacity by 440,000 tons within a year. The ore is lean, consisting of fine iron oxides in silicate rock. The oxides are magnetic and nonmagnetic but there is a relatively small percentage of magnetite present. Fig. 9 shows the type of magnetic roasting furnace used and Fig. 10 the flowsheet.

In 1925 a rotary kiln furnace was built at Gijon, Spain, but was abandoned in the same year after intermittent operation. It also is described in *Bulletin* 13, page 87.

---

[1] T. Umene: A Brief Description of Magnetic Roasting at Anzan. Translated by T. Abbe. Univ. Minnesota, Mines Expt. Station *Bull.* 13 (May 10, 1937) 72–84.

# Selective Electrostatic Separation

By Herbert Banks Johnson*

(New York Meeting, February, 1938)

During the past 10 or 12 years very little information has been made generally available concerning the commercial possibilities of separating materials by means of static electricity; and yet during that same period important improvements have been made in various branches of the science of electricity, which, when taken together, and applied to electrostatic separation, have resulted in important improvements in that art as well. For example, much improvement has been made in high-voltage electrical equipment such as full-wave vacuum-tube rectification and improved mechanical rectification. Great strides have likewise been made in the development of insulators for high-voltage work, not only in the materials used but also in the design of the insulators themselves. Again, in another field, the development of air-conditioning equipment has improved the technique of controlling the surface condition, through drying or humidifying, of the various materials that are passed through the electrostatic separator.

In many authoritative publications and textbooks, the electrostatic separation process is declared to require a balance far too sensitive for general commercial application. For example, one publication[1] in the past has referred to an unfavorable effect on the process caused by varying atmospheric conditions such as humidity. Some[2] have even gone so far as to state that sunlight and shadows may seriously affect the separating efficiency of the process. Such statements may have been true in the early development of the art, when the source of static electricity was derived from a friction disk machine, such as the Wimshurst. The Blake Mosher equipment and the work of Huff in applying motor-generator sets, transformers and mechanical rectification overcame much of this kind of objection to the commercial application of the electrostatic separating process.

Another objection made periodically is that it is generally considered necessary to feed the particles into the electrostatic field in a stream that

---

Manuscript received at the office of the Institute Nov. 5, 1937. Issued as T.P. 877 in Mining Technology, January, 1938.

* Vice President, Ritter Products Corporation, Subsidiary of Ritter Dental Manufacturing Co., Ritter Park, Rochester, N. Y.

[1] Wiard: Theory and Practise of Ore Dressing, 412. 1915.

[2] Liddell: Handbook of Non-Ferrous Metallurgy, 1, 178. 1926.

is only one particle deep. Since it is generally true that materials coarser than 6 mesh do not lend themselves to separation by the electrostatic process, it is easily seen that in order to obtain commercial volumes and capacity in the electrostatic separator, the feeding surface of the machine would have to be very large. This would involve large and expensive machines, which would also consume impractical amounts of floor space—and this objection becomes all the greater when one considers that while 6 mesh is perhaps the limit of coarseness, many materials as fine as 200 mesh are susceptible to separation by means of the electrostatic process, the average size being probably around 80 mesh.

## Electrostatic Conductivity

For the past several years the writer has been investigating the possibilities of applying the electrostatic process of separation to various materials and problems that are outside of the usual mining and concentration fields. In the course of this work, a thoroughly modern laboratory was built in which was assembled much of the new equipment already referred to. More recently, owing largely to the discoveries made while working on other materials, the writer returned to minerals to undertake some intensive research. The object of this investigation was to assemble the latest developments in electrical equipment, insulating materials and mechanical improvements and to combine them in such manner as to develop more accurate information concerning the behavior of minerals in an electrostatic field and to provide a means of comparison by measuring the electrostatic conductivity of various minerals in terms of voltage. The results, of course, are relative and not absolute, because the readings are in terms of voltage only and not in terms of the strength of the electrostatic field. The results, however, are truly relative because the only variable was the voltage, the distance between the electrodes, which is the other factor in the strength of an electrostatic field, being kept constant, as will appear below from the description of the machine that was used.

It should be further emphasized that what was being investigated was the relative *electrostatic conductivity* of various minerals. Perhaps the use of the word "conductivity" is misleading because what is meant is not the relative ease or resistance of the various minerals to the passage of electrical current through them but rather the relative susceptibility of the minerals to being affected by a static charge or field.

For the purpose of this investigation, a full-wave, high-voltage tube rectifier was used, which was specially designed to give very close voltage control so that increases in the voltage could be made in very small steps. A special separator was designed, equipped with electrode insulators made of material capable of insulating against 60,000 volts and of exterior design that gives the greatest protection against surface leaks from the charged electrode. Fundamentally, the separator was very simple and can be represented schematically as in Fig. 1, in which *A* is a hopper from which the material is fed by revolving roll *B* into the electrostatic field created between *B* and the revolving charged electrode *C*. The line, *DE*, which is tangent to roll *B*, represents the line of gravity fall; that is, the line on which the material would fall from roll *B* if there were no other force acting upon it except gravity. Roll *B*, it is true, is revolving at 25 r.p.m., but this speed is so slow that for the purpose of this work the centrifugal force is a negligible factor. Roll *B*, it can be seen, performs a dual function—it conveys the material into the static field and at the same time acts as one of the electrodes of the field. Hence *B* is termed the "material-conveying electrode" and *C* the "charged electrode." *B* is usually grounded, while *C* is positively charged with static electricity from the high-voltage vacuum-tube rectifier. The machine was so constructed that the charged electrode *C* was permanently fixed in one position with relation to roll *B*. This, of course, was necessary because the strength of the static field between *B* and *C* could be varied by keeping the voltage on *C* constant and moving *C* closer to *B* or farther away from it. The purpose of the investigation, as stated already, was to compare the electrostatic conductivity of the various minerals in terms of voltage, therefore it was necessary to keep the distance between *B* and *C* constant and to vary the strength of the electrostatic field simply by varying the voltage on *C*. *F* is a dividing gauge permanently set in such a position that the line is 3/16 in. in front of the line *DE*.

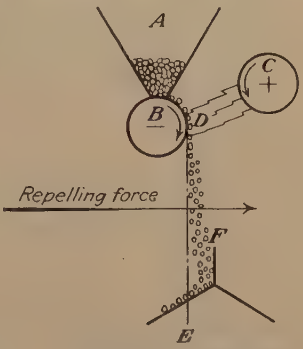


Fig. 1.—First arrangement of separator.

## Testing Procedure

The technique of the investigation was to put the mineral to be observed in the hopper *A* with the material-conveyor roll *B* revolving at 25 r.p.m., so as to convey the material out of the hopper. No static electricity was supplied to the revolving electrode *C*, so that the stream of particles fell approximately in the line *DE*. A low static voltage was then applied to the electrode *C* and the voltage was gradually increased until all the particles in the stream were observed to be deflected away from the line of gravity fall and until the front of the stream just touched the dividing gauge *F*. The voltage necessary to deflect each stream of minerals to this extent was then recorded. This procedure was followed for each of the 90 minerals investigated. Each mineral was also investigated by this method several times under varying atmospheric conditions to check the results.

The minerals used in the investigation were obtained from Ward's Natural Science Establishment, Inc., at Rochester, N. Y. They were all carefully selected for their purity and when associated minerals and gangues were present the mineral was previously separated by the electrostatic process to obtain a purer material for the purpose of the investigation.

The mineral samples were all crushed to pass through a 16-mesh screen. They were then screened on 150 mesh to eliminate all particles smaller than that size. Thus the sizes of the particles in these tests ranged between less than 16 mesh and larger than 150 mesh. This size was selected because it was considered to be representative of the great majority of commercial separation possibilities. The minerals were heated to approximately 175° F. and dried immediately before being placed in the hopper for observation in the electrostatic field. This procedure was followed to assure uniformity in surface moisture in all the minerals and thus to get accurate comparisons of the electrostatic voltage required to deflect the stream as described above.

As has been mentioned, after all the minerals had been observed once, the test was repeated several times to check the voltage readings under different weather conditions, once during dry weather with low humidity conditions and again during wet weather with high humidity conditions. Practically no difference was found in the action of the minerals in the electrostatic field or in the voltage required to deflect the stream the fixed amount as described, as long as the surface of the minerals was dry while passing through the machine. Apparently, internal moisture content, which varies considerably, does not affect the conductivity as long as the surface is dry during the time that the particles are in the electrostatic field.

No difference was observed in the behavior of the minerals in the electrostatic field, whether operating in a very strong sunlight or complete darkness, as long as the surface moisture and the voltage were constant.

The depth of the stream of minerals—that is, whether one particle in thickness or three or four particles in thickness—as it was fed into the electrostatic field had no observable effect on the action of the stream in the field.

## INFLUENCE OF ELECTROSTATIC FIELD

During the tests, it was observed that some of the minerals—mainly those of nonmetallic character such as silicates, carbonates, and oxides of silicon—had a strong tendency to adhere either to the positively charged or to the negatively charged electrode and that these minerals behaved differently from the others while in the influence of the electrostatic field. It was immediately evident that this peculiar action would seriously interfere with the efficient separation of a great many mineral combinations that are involved in general concentrating work.

In order to determine the implications of this observation for separation possibilities, the machine as described in Fig. 1 was altered by moving the dividing gauge *F* until it just touched the front of the stream falling freely by gravity alone from the material-conveying electrode *B* (Fig. 2). Thus the machine was set in the conventional fashion for an electrostatic separator.

The next step was to pass some calcite through the separator. This mineral, instead of being repelled from the negatively charged material-conveying electrode *B*, or instead of falling in the line of gravity *DE*, seemed to be repelled behind the line of gravity and away from the positively charged electrode *C*. Silica, which is often associated with calcite, was passed through the separator, but it was repelled over the dividing gauge in the usual manner.

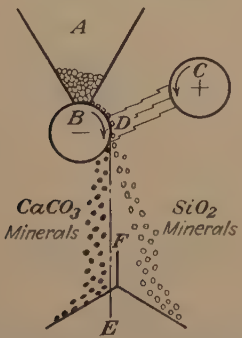


FIG. 2.—SECOND ARRANGEMENT OF SEPARATOR.

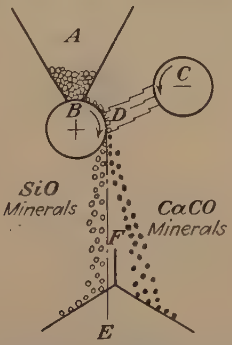


FIG. 3.—REPELLING EFFECT ON CALCITE AND SILICA WITH REVERSED POLARITY OF ELECTRODES.

The polarity of the two electrodes was then interchanged or reversed, the revolving electrode *C* being charged negatively while the material-conveying electrode *B* was positively charged. The same minerals were again passed through the separator but in this instance the repelling effects were observed to be interchanged (Fig. 3). That is, the calcite was repelled from the material-conveying electrode (now positively charged) and over the dividing gauge while the silica was repelled away from the revolving electrode *C* (now negatively charged) and behind the line of gravity fall.

It was then necessary to pass all of the minerals that had been observed in the first investigation through the separator, to test them for what has been termed "reversibility." It was found that the majority of the minerals were not susceptible to any interchange of the polarity of the electrodes; that is, they would be repelled away from the material-conveying electrode *B* and over the dividing gauge *F* regardless of whether the electrode was positively charged or negatively charged. In Table 1, such minerals are designated as "nonreversible." On the other hand, the majority of the silicates, carbonates and oxides of silicon (that is, those that were mentioned above to have been observed to be adhering to one or the other of the electrodes) were found to be "reversible," and are so designated in the table. The minerals that are always repelled from the positive electrode are marked *RP* (repelled or reversible positive) while those that are always repelled from the negative electrode are marked *RN* (repelled or reversible negative).

To the writer, at least, this phenomenon was entirely new and offered new possibilities in the electrostatic control of minerals. No final explanation of the phenomenon is offered except to state that if it could be shown that some of the mineral particles have a natural electrical charge that is either positive or negative it would meet the case. Whatever the explanation, the discovery of this phenomenon offers definite means of improving the practical separation by the electrostatic process of a combination of minerals in which it is known that one is "reversible."

## ELECTROSTATIC REVERSIBILITY

The discovery of the electrostatic reversibility of these minerals completely changes the value of all previously published lists of electrostatic conductors and nonconductors. In the past, an electrostatic conductor was one that was repelled over the dividing gauge and away from the material-conveying electrode. On this basis quartz, fluorspar and calcite have always been listed as nonconductors.[3] By interchanging or reversing the polarity of the electrodes, however, it has been shown how these minerals can be readily repelled over the dividing gauge and thus be considered as good conductors.

Table 1 may be used as a reference when considering the possibility of applying the latest electrostatic equipment to commercial separating problems. To facilitate the use of this list, the 90 minerals have been numbered. They have also been divided into groups, such as Native Elements, Sulphides, Haloids, Oxides of Silicon, etc. Each mineral is listed by name in the second column, followed by the chemical formula for its composition. The third column states the geographical location of the field from which this particular sample was obtained. In the fourth column is recorded the electrostatic voltage required to deflect the stream of the mineral a given amount under the circumstances of the test. This was fully explained earlier in the paper.

In the last column is a notation as to whether or not the mineral is susceptible to reversibility. If it is susceptible to reversibility, it is further designated as "Reversible Positive" or "Reversible Negative." A mineral designated in this column as "RN" indicates that it is reversible negative; that is, it is always repelled from the negatively charged electrode. On the other hand, a mineral noted as "RP" indicates that it is reversible positive; that is to say, it is always repelled from the positively charged electrode. A mineral that is designated in this column as "Non" is not reversible.

---

[3] Ref. 1, 413.

It is interesting that, with one exception, sulphur, all the native elements tested were found to be nonreversible. The voltage required in this group varied from 2800 for flake graphite, which is very nearly pure carbon, to 10,920 volts for sulphur. As far as reversibility is concerned, a similar condition is found in the sulphide group. All of these were found to be nonreversible except sphalerite, which was repelled in every test from the negative electrode. The voltage range was comparatively narrow, from 4680 for bornite and chalcopyrite to 8580 for sphalerite. It is interesting that the one mineral in both the sulphide group and the native element group that is susceptible to reversibility required the highest voltage in its respective class.

Only three haloids were tested, and of these halite and fluorite were found to be nonreversible while cryolite was found to be reversible positive. The voltage range was from 4056 for halite to 5460 for cryolite. Again the mineral in the group requiring the highest voltage was the one that was reversible.

All of the seven variations of quartz tested were found to be reversible negative. As a group they all required relatively high voltage, the range being from 8892 to 14,820.

The three oxides of metals tested were nonreversible. Corundum required a voltage of 13,728 and hematite and ilmenite required voltages of 6240 and 7020, respectively. With these conditions, it might be expected that corundum would be reversible but it did not prove to be so in the actual experiments.

In the group of intermediate oxides, only one, bauxite, was found to be reversible. This mineral, however, required the maximum voltage for the group—namely, 8580—but limonite, which was nonreversible, required the same voltage. The lowest voltage found in this group was 4680 for pyrolusite.

The carbonates tested showed very mixed results. Five were found to be reversible positive; one, reversible negative and the remaining two nonreversible. While four of the reversible carbonates required a high voltage, two that were also reversible required voltages in one case exactly the same and in the other very nearly the same as the two nonreversible carbonates. Two samples of calcite were investigated, one coming from Montana and one from Missouri. No difference on the basis of geographical origin was discovered.

### TABLE 1.— *Mineral Conductivity*

| No. | Mineral and Chemical Composition | Source | Voltage | Reversible[a] |
|---|---|---|---|---|
| NATIVE ELEMENTS | | | | |
| 1 | Flake graphite, C | Texas | 2,800 | Non |
| 2 | Graphite-plumbago, C | Ceylon | 3,588 | Non |
| 3 | Sulphur, S | California | 10,920 | RP |
| 4 | Arsenic, As | Canada | 6,552 | Non |
| 5 | Antimony, Sb | California | 7,800 | Non |
| 6 | Bismuth, Bi | Canada | 4,680 | Non |
| 7 | Silver ore, Ag | Cobalt | 6,552 | Non |
| 8 | Iron in basalt, Fe | Germany | 7,800 | Non |
| SULPHIDES OF THE SEMIMETALS | | | | |
| 9 | Stibnite, $Sb_2S_3$ | Nevada | 6,864 | Non |
| 10 | Molybdenite, $MoS_2$ | Colorado | 7,020 | Non |
| 11 | Galena, PbS | Oklahoma | 6,864 | Non |
| 12 | Chalcocite, $Cu_2S$ | Alaska | 6,552 | Non |
| 13 | Sphalerite, ZnS | Oklahoma | 8,580 | RN |
| 14 | Niccolite, NiAs | Cobalt | 7,800 | Non |
| 15 | Pyrrhotite, $Fe_5S_6$ to $Fe_{16}S_{17}$ | Canada | 6,552 | Non |
| 16 | Bornite, $Cu_5FeS_4$ | Transvaal | 4,680 | Non |
| 17 | Chalcopyrite, $CuFeS_2$ | Arizona | 4,680 | Non |
| 18 | Pyrite, $FeS_2$ | Utah | 7,800 | Non |
| 19 | Smaltite, $CoAs_2$ | Canada | 6,396 | Non |
| 20 | Marcasite, $FeS_2$ | Oklahoma | 5,460 | Non |
| HALOIDS | | | | |
| 21 | Halite, NaCl | Prussia | 4,056 | Non |
| 22 | Fluorite, $CaF_2$ | Illinois | 5,148 | Non |
| 23 | Cryolite, $Na_3AlF_6$ | Greenland | 5,460 | RP |
| OXIDES OF SILICON | | | | |
| 24 | Quartz, chert, $SiO_2$ | Missouri | 8,892 | RN |
| 25 | Quartz, smoky, $SiO_2$ | Colorado | 9,672 | RN |
| 26 | Quartz, flint, $SiO_2$ | England | 10,140 | RN |
| 27 | Quartz, gold, $SiO_2$ | Dakota | 10,140 | RN |
| 28 | Quartz, crystal, $SiO_2$ | Brazil | 13,416 | RN |
| 29 | Quartz, milky, $SiO_2$ | Pennsylvania | 14,820 | RN |
| 30 | Quartz, rose, $SiO_2$ | S. Dakota | 14,820 | RN |
| OXIDES OF METALS | | | | |
| 31 | Corundum, $Al_2O_3$ | Transvaal | 13,728 | Non |
| 32 | Hematite, $Fe_2O_3$ | England | 6,240 | Non |
| 33 | Ilmenite, $FeTiO_3$ | India | 7,020 | Non |
| INTERMEDIATE OXIDES | | | | |
| 34 | Magnetite sand, $FeO.Fe_2O_3$ | California | 7,800 | Non |
| 35 | Franklinite, (Fe, Zn, Mn)O.(Fe, Mn)$_2$O$_3$ | New Jersey | 8,112 | Non |
| 36 | Chromite, $FeCr_2O_4$ | S. Rhodesia | 5,616 | Non |
| 37 | Rutile, (TiO)$TiO_3$ | Virginia | 7,332 | Non |
| 38 | Pyrolusite, $MnO_2$ | New Mexico | 4,680 | Non |
| 39 | Manganite, MnO(OH) | California | 5,616 | Non |
| 40 | Limonite, $2Fe_2O_3.3H_2O$ | Alabama | 8,580 | Non |
| 41 | Bauxite, $Al_2O_3.2H_2O$ | Tennessee | 8,580 | RN |
| CARBONATES | | | | |
| 42 | Calcite, $CaCO_3$ | Montana | 10,920 | RP |
| 43 | Calcite $CaCO_3$ | Missouri | 10,920 | RP |
| 44 | Dolomite, $CaMg(CO_3)_2$ | New York | 8,268 | RP |
| 45 | Magnesite, $MgCO_3$ | Greece | 8,580 | RP |
| 46 | Siderite, $FeCO_3$ | Connecticut | 7,176 | Non |
| 47 | Rhodochrosite, $MnCO_3$ | Montana | 8,580 | Non |
| 48 | Smithsonite, $ZnCO_3$ | New Mexico | 12,480 | RN |
| 49 | Aragonite, $CaCO_3$ | California | 14,800 | RP |
| SILICATES | | | | |
| 50 | Microcline, $KAlSi_3O_8$ | Canada | 7,488 | Non |
| 51 | Oligoclase, $n(NaAlSi_3O_8)M(CaAl_2Si_2O_8)$ | N. Carolina | 6,240 | RN |
| 52 | Labradorite, $(NaAlSi_3O_8)(CaAl_2Si_2O_8)_3$ | Labrador | 4,992 | Non |
| 53 | Enstatite, $MgSiO_3$ | Transvaal | 7,800 | RN |
| 54 | Pyroxene, $RSiO_3$ | Canada | 6,084 | RN |
| 55 | Amphibol-hornblende, $Ca(Mg,Fe)_3(SiO_3)_4$ | Canada | 7,020 | RN |
| 56 | Nephelite, $K_2Na_6Al_8Si_9O_{34}$ | Canada | 6,240 | Non |
| 57 | Garnet, $R_3R_2(SiO_4)_3$ | New York | 18,000 | Non |
| 58 | Rhodolite, $2Mg_3Al_2(SiO_4)_3Fe_3Al_2(SiO_4)_3$ | N. Carolina | 16,380 | RP |
| 59 | Almandite, $Fe_3Al_2(SiO_4)_3$ | New York | 12,480 | Non |

TABLE 1.—(*Continued*)

| No. | Mineral and Chemical Composition | Source | Voltage | Reversible[a] |
|---|---|---|---|---|
| SILICATES (*Continued*) | | | | |
| 60 | Chrysolite, $(Mg, Fe)_2SiO_4$ | N. Carolina | 9,204 | RP |
| 61 | Zircon, $ZrSiO_4$ | N. Carolina | 11,700 | RN |
| 62 | Topaz, $(AlF)_2SiO_4$ | Virginia | 12,480 | RP |
| 63 | Kyanite, $Al_2SiO_5$ | Connecticut | 9,204 | Non |
| 64 | Axinite, $H(Ca, Fe, Mn)B(Al, Fe)_2(SiO_4)_4$ | France | 10,296 | RN |
| 65 | Calamine, $H_2Zn_2SiO_5$ | Missouri | 9,048 | Non |
| 66 | Tourmaline, $H_9Al_3(B.OH)_2Si_4O_{19}$ | California | 7,176 | RN |
| 67 | Muscovite, $(H, K)AlSiO_4$ | Pennsylvania | 2,964 | RP |
| 68 | Lepidolite, $(OH, F)_2KLiAl_2Si_3O_{10}$ | S. Dakota | 4,992 | Non |
| 69 | Biotite, $H_2K(Mg, Fe)_2Al(SiO_4)_3$ | Canada | 4,836 | Non |
| 70 | Serpentine, $H_4Mg_3Si_2O_9$ | New York | 6,084 | RP |
| 71 | Talc, $H_2Mg_3(SiO_3)_4$ | N. Carolina | 6,552 | Non |
| 72 | Kaolinite, $H_4Al_2Si_2O_9$ | S. Carolina | 6,708 | RN |
| 73 | Bentonite | Wyoming | 3,588 | Non |
| PHOSPHATES | | | | |
| 74 | Monazite Sand, $(Ce, La, Di)PO_4$ | N. Carolina | 6,552 | Non |
| 75 | Apatite, $(CaF)Ca_4(PO_4)_3$ | Canada | 11,700 | RP |
| SULPHATES | | | | |
| 76 | Barite, $BaSO_4$ | S. Carolina | 5,772 | Non |
| SULPHATES (*Continued*) | | | | |
| 77 | Anhydrite, $CaSO_4$ | N. Brunswick | 7,800 | RP |
| 78 | Gypsum, $CaSO_4.2H_2O$ | Michigan | 7,644 | RP |
| TUNGSTATES-MOLYBDATES | | | | |
| 79 | Wolframite, $(Fe, Mn)WO_4$ | England | 7,332 | Non |
| 80 | Scheelite, $CaWO_4$ | Nova Scotia | 8,580 | Non |
| 81 | Wulfenite, $PbMoO_4$ | New Mexico | 11,700 | Non |
| HYDROCARBON COMPOUNDS | | | | |
| 82 | Anthracite | Pennsylvania | 3,588 | Non |
| 83 | Bituminous coal | Pennsylvania | 4,056 | RP |
| 84 | Bituminous coal, coking | Virginia | 6,240 | RP |
| ARTIFICIAL ABRASIVES | | | | |
| 85 | Aluminous oxide | New York | 13,572 | RP |
| 86 | Silicon carbide | New York | 5,616 | Non |
| BEACH SANDS | | | | |
| 87 | Rutile | Australia | 7,488 | Non |
| 88 | Zircon | Australia | 11,076 | RP |
| 89 | Rutile | India | 8,892 | Non |
| 90 | Zircon | India | 11,076 | RP |

[a] Non, not reversible.
RP, reversible positive.
RN, reversible negative

Twenty-four silicates were examined and the results were very mixed. Five were found to be reversible positive; eight to be reversible negative and the remaining eleven to be nonreversible. The findings with regard to voltage were also mixed, for the silicates that were reversible positive included both the highest, with one exception, and the lowest voltage for the entire group. These were, respectively, rhodolite with a voltage of 16,380 and muscovite with a voltage of 2964. The other voltages for the silicates reversible positive were 12,480 for topaz, 9204 for chrysolite and 6084 for serpentine. For the silicates that were found to be reversible negative, the voltages were all fairly close together—around an average of 6500—except zircon at 11,700 and axinite at 10,296. The actual range for silicates, except zircon and axinite, that were reversible negative was found to be from 6084 for pyroxene to 7800 for enstatite. The nonreversible silicates required a voltage varying from 18,000 for garnet to 3588 for bentonite.

Monazite sand and apatite were the only phosphates tested. Monazite sand was found to be nonreversible and required a voltage of 6552 while apatite was found to be reversible positive and required a voltage of 11,700.

Of the three sulphates examined, two—anhydrite and gypsum—were found to be reversible positive and required a difference in voltage of only 156 volts. Barite was found to be nonreversible and required a voltage of 5772.

Wolframite, scheelite and wulfenite were all found to be nonreversible and required voltages of 7332, 8580 and 11,700, respectively.

In examining the hydrocarbon compounds, it was found that anthracite having a voltage of 3588 was nonreversible while bituminous coal, which required only 468 volts more than anthracite, was found to be reversible positive. Bituminous coal suitable for coking required 6240 volts and was also reversible positive. Because of the close voltage requirements between anthracite and bituminous coal, it would ordinarily be impossible to obtain a separation but, because bituminous coal was found to be reversible positive while anthracite was nonreversible, a separation would theoretically be possible. To confirm this theory, anthracite and bituminous coal were thoroughly mixed together and were run through the separator, which was set in such a way as to take advantage of the fact that bituminous coal was reversible positive. When the analysis of the resulting separation was made, it was found that the anthracite was concentrated in one product and the bituminous coal in the other.

Two artificial abrasives were inspected. Aluminous oxide was found to be reversible positive at a voltage of 13,572 while silicon carbide was nonreversible at a voltage of 5616.

Australian beach sand, composed of rutile and zircon, and similar beach sand from India were tested. In both the zircon was found to be reversible positive at a voltage of 11,076 while the rutile was nonreversible, with a voltage of 7488 for that which came from Australia and 8892 for that which came from India. It is interesting to note that zircon from North Caroline had been tested among the silicates (No. 61) and while the voltage for the North Carolina mineral was only 624 volts higher than the zircon found in the beach sands of Australia and India, yet the North Carolina specimen was found to be reversible negative while that found in the beach sands was reversible positive.

In the subsequent experiments with the machine set as a separator, using these and other minerals, it was found that a difference of 3000 volts usually assures a fair degree of separation on materials at close sizing, while a difference of 5000 volts usually assures a very good separation even on unsized materials. For example, flake graphite with a voltage reading of 2800 can be easily separated from sulphur having a voltage of 10,920; or anthracite, with a voltage of 3588, can be separated easily from most carbonates and oxides of silicon. Virtually a perfect separation can be made of rutile at 7488 and zircon at 11,076. Furthermore, if it is desired to separate two minerals of which the respective relative voltages are shown in the table to be close together, a separation may still be possible provided one of the minerals is reversible at one sign and the other reversible at the opposite sign, or provided one is reversible and the other is nonreversible. Perhaps the most interesting example of the phenomenon has already been given in the separation of anthracite and bituminous coal, where the difference in voltage is only 532 and yet a separation is possible because anthracite is nonreversible and bituminous coal is reversible positive.

The results of these investigations and Table 1 are being made known now in the hope that they may be of benefit to the engineering profession and industry in helping to solve, by means of improved electrostatic equipment, some of the baffling separation problems that sometimes are all that stand in the way of passing on to the consuming public the benefits of recent research and discovery.

## DISCUSSION

*(Arthur F. Taggart presiding)*

F. Fraas* and O. C. Ralston,† College Park, Md. (written discussion).—The improvements reported by Mr. Johnson over the older electrostatic separation are gratifying. His new classification of minerals as reversible positive, reversible negative or irreversible, is convenient but remains unexplained and clouded with mystery.

---

* Assistant Chemist, U. S. Bureau of Mines.

† Chief Engineer, Nonmetals Division, U. S. Bureau of Mines.

Mr. Johnson speaks of "electrostatic conductivity," or relative susceptibility to electrostatic fields, but this phenomenon is really made up of two variables. In more conventional terms, these are the true electrical conductivity and contact potential.

Later we hope to discuss the more important electrostatic separation processes of the past in the light of the same considerations, but at present we shall consider only Mr. Johnson's new and improved process as compared to its earlier Huff ancestor, for the purpose of pointing out the complicating effects due to contact potentials. Probably every electrostatic separation process of the past has been complicated with the effects of contact potential or frictional electricity on the separator chutes or rolls. The Nonmetals Division of the Bureau of Mines has had the subject under study for the past year and ultimately will have several communications to publish.

The potential developed when two metals are brought into contact and then separated is called contact potential. We wish to apply the same term to the potential shown when a nonconductor is brought into contact with a metal, or even another nonmetal and then separated. The charge developed at the point of separation cannot rapidly spread as it does on a good conductor, but otherwise we may still postulate an electron pressure or electron configuration of the solid crystalline lattice or of the elements of which it is built up. Permit a nonconductive mineral particle to slide down a surface and it will build up charge from the fundamental contact potentials, which are not easily discharged or neutralized, owing to the low conductivity of the mineral particle. A conductive mineral sliding over a conductive surface cannot build up a very effective contact potential into a multiplied frictional electric charge. We expect to describe ultimately several electrostatic separators that we have developed, in which charges are definitely built up through contact potential under more definitely known and controlled conditions.

We now propose to bring out a clearer view of Mr. Johnson's effects through appeal to this distinction between contact potential and electrical conductivity. In his Table 1, the minerals classified as reversible positive and reversible negative are all nonconductors, whereas those classed as nonreversible are conductors or have such a low contact potential with the metal used for "material-conveying electrode" that any slight existing conductivity will be the controlling factor. Since Mr. Johnson has his minerals contacted with metal roll and in addition has a superposed electrical field, there exists a competition between the charging by contact potential and the charging by conductivity in conjunction with the superposed electric field.

The minerals given in Table 1 as "reversible positive" are in reality those that are positive with respect to the conveying electrode as a result of contact potential. In a similar manner those listed as "reversible negative" are negative with respect to the conveying roll. The nonreversible minerals are charged by virtue of their true electric conductivity and the gradient of the superposed electrical field, which draws the charges out on the particles. On the basis of our work it is possible to explain the discrepancies that occur in Mr. Johnson's data. For example, zircon 61 is negative with respect to the conveying electrode because this is the normal potential for clean zircon from crushed ore. Zircon 88, from beach sand, is positive because of accumulated films of (probably) organic matter. Aluminum oxide is positive as a normal potential whereas bauxite is negative, owing to films of adsorbed silica and kaolin. Halite, like c.p. sodium chloride, should be highly positive, but we have found that the naturally occurring mineral from Carlsbad, New Mexico, is negative. This is probably because of adsorbed silica, since the sylvite occurring with our halite is red in color, similar in appearance to the coprecipitated $SiO_2$ and $Fe_2O_3$ prepared in the laboratory and found in nature.

Mr. Johnson states that humidity has no effect on his separations, but this is because he heats his minerals to 175° F. and consequently a high humidity, at, say

80° F., is a low humidity at 175° F., and therefore all his experiments were carried out under very dry conditions.

One fact we should like to know is the spacing of the electrodes to which the recorded potentials were applied. This is necessary in order to figure the potential gradient.

Another question is: Why did the Huff and former electrostatic separations languish almost to the vanishing point, as far as mineral separations are concerned?

G. W. Jarman, Jr.,* New York, N. Y. (written discussion).—While the list of minerals as set forth in this paper is extremely interesting from a scientific viewpoint, we wish to raise some questions as to the behavior of these minerals when mixed together, and not treated one by one.

Mr. Johnson made the statement that all the minerals tested were minus 16 plus 150 with no intermediate classification. We have found intermediate classification to be a practical requirement when particles are difficult to separate electrostatically. Our experiments with mixtures of particles have given evidence that in certain cases a particle that responds to a plus sign in one combination of minerals may respond to the opposite sign in another combination.[4]

Mr. Johnson mentions that certain particles stick to the rotor and thus interfere with the separation. We have found that this peculiar action is a benefit; indeed, electrostatic separators that deliberately pin all the particles to the rotor by means of a brush discharge have been designed and placed in operation. The particles lose their charge in accordance with the degree of their surface conductivity; those that lose it rapidly become unpinned and are released from the rotor in front of a dividing knife-edge while those that remain pinned fall later behind the dividing knife-edge.

We agree with Mr. Johnson as to the splendid potentialities of the electrostatic field but our response to the question "Where can electrostatic separation be used?" is somewhat narrower than his. We believe that electrostatic separation can be used most beneficially on materials of relatively high value—that is to say, on concentrates or semiconcentrates—because of the greater capital installation per ton-hour of such equipment.

C. E. Locke,† Cambridge, Mass. (written discussion).—The growth of flotation as an ore-dressing process has had some tendency to draw attention away from other standard processes. The ore dresser should not forget these other processes, and instruction in ore dressing in educational institutions should be broad. At any time a special process may be applicable, and unless all of the methods are included an incorrect idea may arise that a new process has been discovered. This is illustrated by the mention in Mining and Metallurgy for January 1938 of the use of decrepitation and screening for the treatment of spodumene, invented by the U. S. Bureau of Mines staff. That process is described in ore-dressing treatises as an old process. Similar processes that have long been known might be mentioned, such as air separation, centrifugal separation, weathering and magnetic roasting. However, it is always possible to improve the technique of these processes, or the apparatus employing them.

Electrostatic separation is not new. It has been applied to special problems. Operation of the process has had its limitations, and it has been looked upon as rather delicate and requiring careful control. I have followed electrostatic separation for a great many years, and the merit of Mr. Johnson's paper, as I see it, is that it shows beneficial results yielded by the application of research even on old processes. It is never safe to make a general prediction, but as far as can be foreseen at the present time, electrostatic separation will not be able to compete with flotation, or with gravity separation, where flotation or gravity separation can be readily applied to the treatment of an ore. Mr. Johnson has shown that where electrostatic separation is called for the process has been improved and broadened, therefore I wish to congratulate the author on his persistence, and on his developments offering an improved tool to the ore dresser. I should like very much to learn what uses are being made of electrostatic separation today, and which plants are working on ores and on various industrial or other materials.

---

* President, Separations Engineering Corporation.

[4] U. S. Patent No. 1017701, Feb. 20, 1912, and No. 1020063, March 12, 1912.

† Professor of Mining and Ore Dressing, Massachusetts Institute of Technology.

H. B. JOHNSON (written discussion).—I have visited the laboratories of the nonmetallic division, Bureau of Mines, at College Park, Md., and have seen some demonstrations by Mr. Fraas. I am sure that in the near future we shall have interesting and helpful publications.

The more reliable procedure, I believe, is the use of a superimposed charge produced by well-known electrical circuits. If the surface condition of the material to be separated is maintained within reasonable limits, a uniform separation is assured under all normal conditions of humidity in high or low altitudes, wet or dry climates, as confirmed by many commercial installations. Humidity seriously affects any static separation of minerals or other materials when depending upon the pyroelectric properties, frictional charges or contact potentials for separation.

Conductivity as referred to electrostatically involves primarily a surface action and the surface condition of the material to be separated is important. Conditioning methods and reagents have been found that will completely change the behavior of minerals in an electrostatic field. This, however, is a subject for further investigation and probably publication at a later date.

The remarks by Mr. Fraas and Dr. Ralston are confusing because they combine two entirely different subjects, which I believe should be treated separately; namely, *selective electrostatic separation* by subjecting minerals to or passing them through a superimposed electrostatic field of known potential and of known polarity and a second method of separating minerals by means of their *pyroelectric* properties or *frictional electrical charges* accumulated through contact potential with various metals. My paper deals entirely with the first method; that is, the behavior of minerals in an electrostatic field of known potential and known polarity. No reference is made nor is any consideration given to the pyroelectric properties of minerals or the charges developed through frictional contact.

Mr. Fraas and Dr. Ralston declare that the reversible positive and reversible negative minerals in Table 1 are all nonconductors while the nonreversible minerals are conductors. Conductivity lists previously published classify in two groups—good conductors and poor conductors, or conductors and nonconductors. In the preparation of previous lists conductors were minerals easily repelled under a superimposed electrostatic charge while nonconductors were not repelled. In the preparation of these lists, it is my belief that no thought was given to selective polarity. Both calcite and quartz are considered nonconductors.

My research shows that by taking two so-called nonconductors—calcite and quartz—and using a negative polarity on the material-conveying electrode, the quartz is repelled as any good conductor is, while if the polarity is reversed to positive the calcite is repelled, as would be a good conductor, using exactly the same combination of metals in contact with the minerals. This reversibility or change of conductivity susceptibility can be made instantly, repelling one or the other as desired.

Figs. 1, 2 and 3 indicate the method and procedure I used in compiling the new mineral list, involving the use of two rotating electrodes in fixed positions with a superimposed electrostatically charged field of known potential and of known polarity and describe a well-known method of electrostatic separation developed by Blake-Morscher, Huff and myself which has been used commercially for the separation of ores and other materials in various parts of the world.

The spacing of the electrodes used for measuring the potential of the minerals referred to in the new mineral list was ⅞ in. from the periphery of one electrode to the periphery of the other electrode. In other words, a gap of ⅞ in. through which the minerals passed under the influence of a superimposed selective electrostatic charge.

The Huff company's business languished largely on account of the rapid progress made by the flotation method in the mining industry. At that time at least $10,000 was being spent on research and development of the flotation process for every dollar spent by the Huff company for research and development. The Huff business was a highly specialized and comparatively small business depending upon the collection of royalties for income. In 1926 the basic patents began to expire and I decided to liquidate the business for the best interests of the stockholders.

The United States patents referred to by Mr. Jarman describe electrostatic dry-table combinations, I believe. In other words, a dry reciprocating table having charged electrodes suspended over the table top, so that the minerals being separated actually are under the influence of mechanical agitation or gravity separation and static influence. It is reasonable to believe that some difference would be noticed in the behavior of minerals under the dual influence of two well-known concentrating principles.

When using the type of equipment illustrated in Figs. 1, 2 and 3, the behavior of minerals is as described in the new mineral list.

I believe all the electrostatic patents issued to Mr. Jarman's company, the Sutton, Steele & Steele Co., of Dallas, Texas, illustrate electrostatically either the use of dry-table static combinations described in the two patents cited or the use of discharge-point electrodes for sticking the particles to the rotor or revolving material-conveying electrode. I always have been interested in the method of repelling the better conductors from the rotor or revolving material-conveying electrode. We must not confuse entirely different principles of applying an electrostatic charge and the behavior of the minerals under the different principles of operation.

The separation of many minerals at highest efficiency often requires classification into several sizes. My experience, however, indicates that through the use of reversibility separations fewer sizes are required, thereby considerably reducing the separation cost.

I believe that each process has its field of application and that, because the new discovery provides better control, selective electrostatic separation will receive more consideration in the future.

At present electrostatic equipment is used for the separation of abrasive materials, coating of abrasive paper, reclamation of abrasive products, separation of beach sands, zircon-rutile and other minerals. It is being used very effectively for the cleaning of spices, seeds and other food products. Within the next two or three years I believe we shall see several electrostatic plants with separating capacities from 25 to 75 tons per hour and at costs per ton that now are not believed possible.

I believe that there is no likelihood of electrostatic separation broadly replacing flotation, gravity or magnetic separation. I believe it will be used in addition to these methods and that more and more flowsheets will use two or possibly three basic principles of concentration, providing the highest yield at lowest cost.

# Comparative Washing Efficiencies in Cyaniding—The Washing Tray Thickener versus the Conventional Countercurrent Decantation Plant

By Neil O. Johnson,* Junior Member A.I.M.E.

(New York Meeting, February, 1939)

In the cyanidation of gold, silver and mixed ores, the solids suspended in the pulp after fine grinding, primary settling and series agitation are subjected to a washing step known, generally, as countercurrent decantation, abbreviated C.C.D. The conventional C.C.D. plant consists of a series of separate thickeners—three to five in number—arranged in series on slightly different elevations. Solids settled in the first thickener are pumped at maximum density into the second thickener, where they are diluted with weak solution overflowing the third. After settling in the second thickener they are pumped to the third, where the process of repulping with still weaker solution is repeated, and so on throughout the system, until they reach the last thickener and are repulped with barren solution or water.

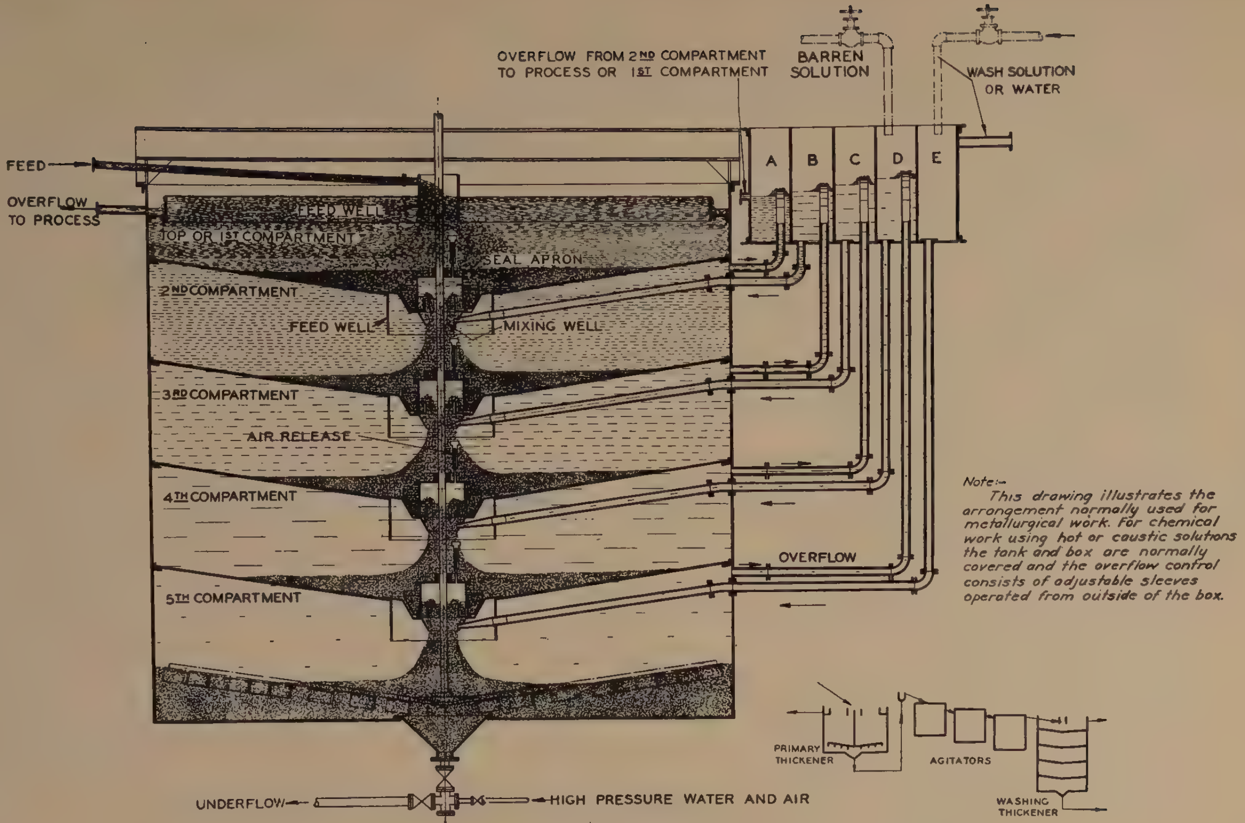
Recently there has been developed a new type of thickener, known as the Dorr Washing Tray Thickener, consisting of up to five individual thickeners, which performs in a single unit all the functions of a conventional C.C.D. plant. Fig. 1 illustrates the essential features. It is a multicompartment tray thickener, in which the trays operate in series instead of in parallel for countercurrent washing. Feed enters the top compartment via a central, semisubmerged feed well. Strong solution overflows into a peripheral launder. Solids settle to the bottom, are raked to the center and flow into the top of the second compartment, directly below, via an inverted cup and seal.

Solids pass downward, compartment by compartment, against a counter flow of wash solution and finally of fresh water. Thus, in accordance with the basic C.C.D. principle, the solids transfer the dissolved metal content to the wash solution and finally are removed by a diaphragm pump from the bottom compartment virtually free of valuable material. Similarly, the wash water, as it flows through the system, becomes increasingly enriched in dissolved metal until it overflows from compartment two and returns to the process.

---

Manuscript received at the office of the Institute March 8, 1939. Issued as T.P. 1082 in Mining Technology, July, 1939.

* Engineer, The Dorr Company, Inc., Chicago, Ill.



*Note:—*
*This drawing illustrates the arrangement normally used for metallurgical work. For chemical work using hot or caustic solutions the tank and box are normally covered and the overflow control consists of adjustable sleeves operated from outside of the box.*

FIG. 1.—ESSENTIAL FEATURES OF DORR WASHING TRAY THICKENER.

The conventional C.C.D. plant and the washing tray thickener have identical aims—the maximum possible recovery of gold-bearing solution—in short, high washing efficiencies. It is the purpose of this paper to compare these two systems, based on comparative tests conducted in 1938 by the author at the mill of the Cactus Mines Co., Mojave, California.

Cactus Mines is the only company at present operating both systems in parallel and so far has offered the only opportunity for direct comparisons under controllable conditions. This is, however, by no means the only washing tray thickener in existence. There are a dozen in cyaniding alone, notably one at Desert Silver Inc., Silver Peak, Nev., operating on a quick-settling granular pulp containing a large amount of primary slime; one at Mountain Copper Co., Shingle Springs, Calif., handling gossan slime, difficult to settle and wash; and another at the Zeibright mine of Empire Star Mines Co., near Emigrant Gap, Calif., washing finely ground pyrite flotation concentrates after cyaniding.

### *Cactus Mines Mill*

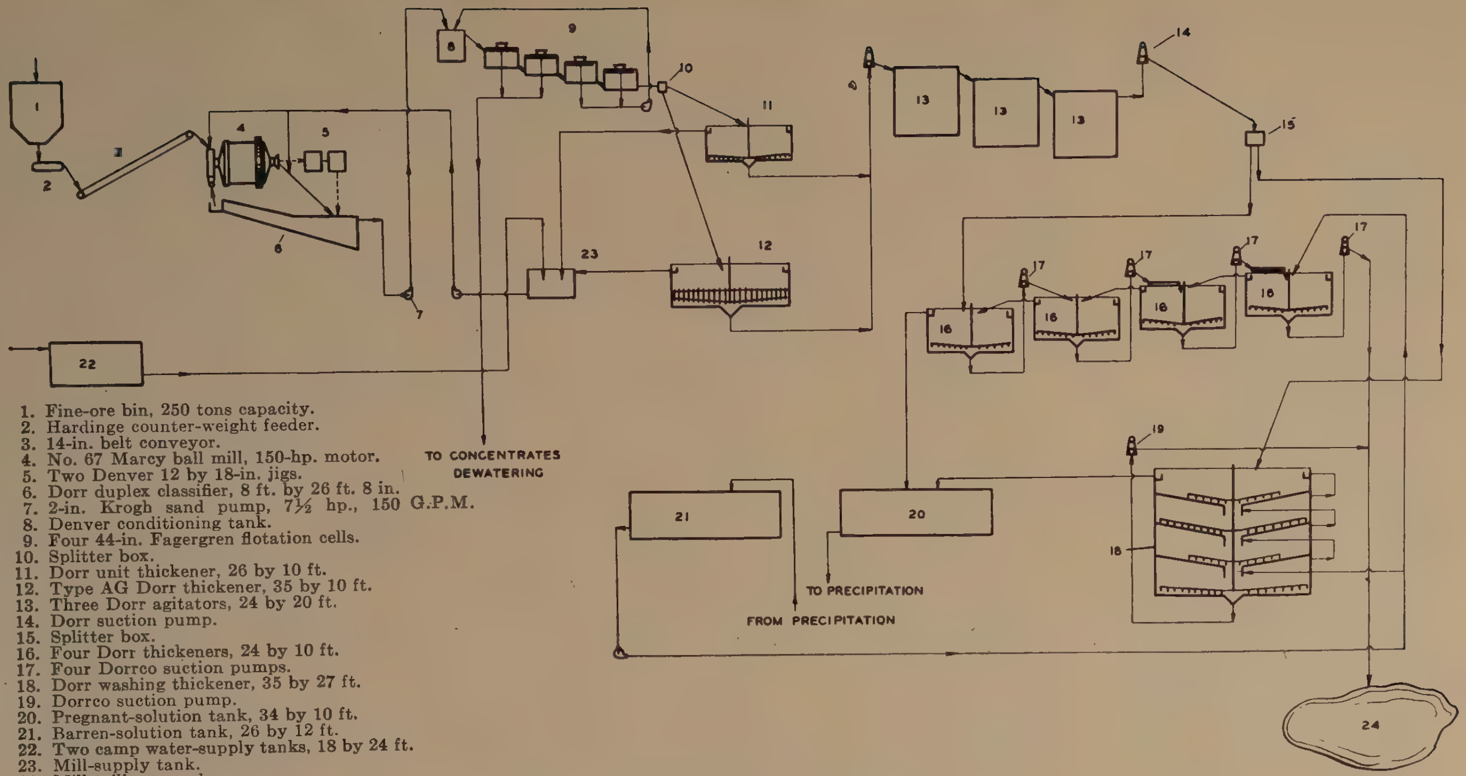
Fig. 2 shows the flowsheet of the Cactus mill. The conventional C.C.D. plant is at the top and the new washing tray thickener installation directly below.

Up to station No. 15, the discharge from the last agitator, the treatment is the same—flotation concentration followed by cyaniding of tailing—and is irrelevant to the scope of this paper. Ore is siliceous, containing both gold and silver, but the gold content alone is considered in this paper, for the sake of simplicity. Grinding is to about 80 per cent minus 200 mesh and rated capacity of the cyanide mill is 125 tons per day.

At station No. 15, the discharge from the last agitator, the cyanide pulp, which is at a dilution of about 2:1, is split. One portion, approximately 40 per cent, flows to a standard C.C.D. system, consisting of four single-compartment Dorr thickeners, 24 ft. in diameter by 10 ft. deep. The other portion, approximately 60 per cent of the total, flows to a four-compartment Dorr washing tray thickener, 35 ft. in diameter by 27 ft. deep.

Tailings from both systems are sent to waste without filtration. Pregnant solutions, overflowing from the first steps in both systems, are sent to the same precipitation plant. Barren solution in measured amounts is returned to both systems for washing purposes. Latham cyanide meters are used for measuring these flows.

The two washing systems are thus in perfect parallel. They receive feed and wash solutions from identical sources. Furthermore, provision was made for accurately measuring and sampling the inputs and outputs—an ideal and seldom attained condition for comparative tests.



1. Fine-ore bin, 250 tons capacity.
2. Hardinge counter-weight feeder.
3. 14-in. belt conveyor.
4. No. 67 Marcy ball mill, 150-hp. motor.
5. Two Denver 12 by 18-in. jigs.
6. Dorr duplex classifier, 8 ft. by 26 ft. 8 in.
7. 2-in. Krogh sand pump, 7½ hp., 150 G.P.M.
8. Denver conditioning tank.
9. Four 44-in. Fagergren flotation cells.
10. Splitter box.
11. Dorr unit thickener, 26 by 10 ft.
12. Type AG Dorr thickener, 35 by 10 ft.
13. Three Dorr agitators, 24 by 20 ft.
14. Dorr suction pump.
15. Splitter box.
16. Four Dorr thickeners, 24 by 10 ft.
17. Four Dorrco suction pumps.
18. Dorr washing thickener, 35 by 27 ft.
19. Dorrco suction pump.
20. Pregnant-solution tank, 34 by 10 ft.
21. Barren-solution tank, 26 by 12 ft.
22. Two camp water-supply tanks, 18 by 24 ft.
23. Mill-supply tank.
24. Mill-tailings pond.

FIG. 2.—FLOWSHEET OF CACTUS MILL.

The conventional C.C.D. plant was installed in 1937, the washing tray thickener in 1938 when it was desired to increase cyaniding capacity from 50 to 125 tons per day. A single washing tray thickener was selected in preference to the same capacity in a four-thickener C.C.D. series, because the total cost of the tray unit on an erected basis was 25 per cent less than the cost of the C.C.D. plant, even without giving weight to the advantages of 75 per cent less ground area, 75 per cent less connected horsepower, only one sludge pump to control instead of four, one foundation instead of four and an over-all greater simplicity of control and sampling.

## TEST PROCEDURE

For the purpose of comparing the washing efficiencies of the two units, it was desirable to maintain equal pulp volumes in both series, so that the additional dissolution that always takes place to a greater or lesser extent in the C.C.D. thickeners would be the same in both. Settling areas were therefore not comparable, but experience has shown approximately equal capacities per square foot in the washing thickener as in the single tank unit. The dissolution in each unit was kept constant, or nearly so, by splitting the feed and the wash solutions to each system in proportion to their active volumes. To do this, Latham cyanide meters were installed for measuring the amount of wash solution and weirs were used to proportion the amount of pulp to each unit. The pulp-distribution weir was checked at regular intervals.

The active volume of the washing tray thickener was 60 per cent and of the C.C.D. system was 40 per cent of the total active volume of 39,224 cu. ft. Consequently, 60 per cent (76.5 tons) of the total feed was split to the former and 40 per cent (51 tons) to the latter, total feed at the time of the test being 127.5 tons per day.

Splitting the feed to the two systems in this ratio, the detention period of the pulp in each unit was kept the same. The barren solution was also divided in the same ratio. This gave the pulp in each system the same amount of barren solution per ton of solids.

At all times the underflow density of the pulp was carried as thick as possible, so that any variable from this source would be eliminated. In following the above procedure, the two units were found to be comparable in two respects: (1) they had the same values of overflow solution; (2) they had the same values in their underflow residues.

The square feet of settling area in the two units are not in the same ratio, 60:40, as are the volumes, detentions and feed rates. In the washing tray thickener the total settling area is 961 sq. ft. and that of the C.C.D. unit is 452 sq. ft., a ratio of 68 to 32. This, however, is of no consequence in these particular tests, which were concerned only with washing efficiency as function of volume, or detention, and number of washing steps, not relative capacity, a function of the settling area provided.

The tests were run April 1 to May 7, 1938. The data reported in this paper were obtained during the seven-day period Apr. 24 to Apr. 30.

## TEST DATA

Table 1 contains typical mill data for the period Apr. 24 to 30, 1938. The figures given are the averages of daily composites. Gold content of the ore and solutions is alone considered, for the sake of simplicity, although in actual practice a record of the silver content is kept in the mill records.

The solutions discharged with the solids in the underflow of both No. 4 thickener and No. 4 compartment are higher in dissolved gold than the solutions overflowing, for two reasons: (1) additional dissolution of values from the solids, and (2) the difficulty of obtaining complete mixing of the diluting wash solution and original richer solution accompanying it with the solids from the previous decantation step.

TABLE 1.—*Typical Operating Data of Cactus Mill*

| | |
|---|---|
| Dry tons milled daily | 128.0 |
| Cyanide head assay, oz. Au per ton | 0.16 |
| Residue from No. 1 agitator, oz. Au per ton | 0.031 |
| Residue from No. 3 agitator, oz. Au per ton | 0.023 |
| Washed tailings, oz. Au per ton | 0.0206 |
| Unwashed tailings, oz. Au per ton | 0.0254 |
| Dissolution in washing thickener C.C.D., oz. Au per ton | 0.0030 |
| Pregnant solution, oz. Au per ton | 0.0318 |
| Barren solution, oz. Au per ton | trace |
| Feed distribution to C.C.D. systems: | |
| Thickeners, tons | 51.0 |
| Per cent | 40.0 |
| Compartment thickener, tons | 76.5 |
| Per cent | 60.0 |
| Distribution of washing solution: | |
| Thickeners—tons | 218.0 |
| Per cent | 40.1 |
| Compartment thickener, tons | 326.0 |
| Per cent | 59.9 |
| Tons solution precipitated | 607.0 |
| Pulp dilutions: | |
| Classifier overflow | 8.0 |
| Underflow No. 1 dewatering thickener | 1.24 |
| Underflow No. 2 dewatering thickener | 1.21 |
| Agitators | 1.97 |
| No. 4 thickener | 1.26[a] |
| No. 4 compartment | 1.19[b] |

[a] 55.7 per cent moisture.

[b] 54.3 per cent moisture.

Table 2 shows that both units produced overflows and underflows having substantially the same values. The soluble loss, it will be seen, is slightly higher in the tray unit than in the thickener unit.

TABLE 2.—*Comparative Solution and Residue Values*
Assays, Oz. Au per Ton

| | Thickener Unit | Tray Unit |
|---|---|---|
| Overflow solution No. 1 | 0.0344 | 0.0340 |
| Overflow solution No. 2 | 0.0147 | 0.0146 |
| Overflow solution No. 3 | 0.0084 | 0.0077 |
| Overflow solution No. 4 | 0.0033 | 0.0036 |
| Underflow residue No. 4 | 0.0196 | 0.0200 |
| Underflow solution No. 4 | 0.0037 | 0.0046 |

TABLE 3.—*Comparative Efficiencies of the Two Units*

C.C.D. THICKENERS AND REPULPERS

| | | |
|---|---|---|
| Washed tails No. 4 thickener | 0.0196 oz. | = $0.686 per ton ore |
| Underflow solution No. 4 thickener | 0.0037 oz. | = 0.1295 |
| Soluble loss per ton of ore | 1.26 × 0.0037 | = 0.163 |
| Total gold dissolved per ton: | | |
| Agitator No. 1 heads | 0.16 oz. | |
| Agitator No. 3 residue | 0.023 oz. | |
| Dissolved in agitators | 0.137 oz. | = $4.795 |
| Gold dissolved in C.C.D. (0.023–0.0196) × $35 | | = 0.119 |
| Total dissolved | | $4.914 |
| Soluble loss | | 0.163 |
| Total dissolved gold recovered per ton | | $4.751 |
| Percentage recovered | $\frac{\$4.751}{4.914} \times 100$ | = 96.6 per cent |

WASHING TRAY THICKENER

| | | |
|---|---|---|
| Washed tails No. 4 compartment | 0.020 oz. | = $0.700 |
| Underflow solution No. 4 compartment | 0.0046 oz. | = 0.161 |
| Soluble loss per ton of ore | 1.19 × 0.0046 | = 0.1916 |
| Total gold dissolved per ton: | | |
| Agitators | | $4.795 |
| Dissolved in washing thickener (0.023–0.02) × $35 | | = 0.105 |
| Total dissolved | | $4.900 |
| Soluble loss | | 0.1916 |
| Total dissolved gold recovered per ton | | $4.7084 |
| Percentage recovered | $\frac{\$4.7084}{4.9000} \times 100$ | = 96.1 per cent |

Table 3 lists the calculations of the washing efficiencies of the two units. Washing efficiency is the ratio of the total gold recovered to the total gold dissolved in the system, the difference between these two factors being soluble loss in the residues sent to waste. The washing efficiency in the washing tray thickener is 96.1 per cent, only 0.5 per cent less than the washing efficiency of the C.C.D. unit.

TABLE 4.—*Comparative Settling Characteristics*

| C.C.D. System | Area, Sq. Ft. | Area, Per Cent | Feed, Tons per Day | Feed, Per Cent | Settling Area, Sq. Ft. per Ton per Day | Final Densities[a] |
|---|---|---|---|---|---|---|
| Washing thickener........ | 961 | 68 | 76.5 | 60 | 12.6 | 1.19 |
| Individual thickeners..... | 452 | 32 | 51.0 | 40 | 8.9 | 1.26 |

[a] Ratio of liquid to solids by weight.

Table 4 shows comparative feed areas and final densities. As mentioned before, the feed was distributed on the basis of tank volumes to equalize for additional dissolution by giving the solids the same time of contact in both units. The final density is somewhat greater in the tray unit, which is to be expected because of the larger settling area available. Were the feed rate adjusted to give the same tons of solids per square foot of area, approximately the same final density would be expected from both units.

## FURTHER SAMPLING

Normally, this would have completed the test work and yielded all the data necessary to make technical and economic comparisons of the two units. However, a further sampling was made to determine the amount of the dissolution of gold taking place in the different steps of the system as reported in Table 5. These determinations were made on the C.C.D. unit only, because it was impossible to obtain pulp samples between the compartments of the washing tray thickener.

Usually the maximum additional dissolution in a C.C.D. system is in the first thickener following agitation and this dissolution gradually decreases in succeeding thickeners. However, as shown in Table 5, by far the greatest dissolution took place in the second thickener. Confirmation of this is indicated in the difference in overflow and underflow solution assays in this thickener. The total additional dissolution of gold in the C.C.D. series amounts to 17.8¢ per ton in the test recorded in Table 5 as compared to 10.5¢ per ton in Table 1, covering a week's composite samples.

TABLE 5.—*Dissolution of Gold during Pulp Washing*

| Material | Au, Oz. per Ton | Cents per Ton Dissolved |
|---|---|---|
| Pulp residues from | | |
| No. 3 agitator | 0.0229 | |
| No. 1 thickener underflow | 0.0224 | 1.7 |
| No. 2 thickener underflow | 0.0184 | 14.0 |
| No. 3 thickener underflow | 0.0178 | 2.1 |
| No. 4 thickener underflow | 0.0187[a] | |
| Total | | 17.8 |
| Solution assays in | | |
| No. 1 thickener underflow | 0.0329 | |
| No. 2 thickener underflow | 0.0156 | |
| No. 3 thickener underflow | 0.0074 | |
| No. 4 thickener underflow | 0.0031 | |

| | Au, Oz. per Ton | | Ratio Water:Solids |
|---|---|---|---|
| Solution assays in | | Pulp dilutions | |
| No. 1 thickener overflow | 0.0327 | No. 3 agitator | 1.95:1 |
| No. 2 thickener overflow | 0.0138 | No. 1 thickener | 1.28:1 |
| No. 3 thickener overflow | 0.0070 | No. 2 thickener | 1.34:1 |
| No. 4 thickener overflow | 0.0026 | No. 3 thickener | 1.30:1 |
| | | No. 4 thickener | 1.19:1 |

[a] Erratic result probably caused by zinc experiments in the precipitation building, faulty sampling, or assaying. Gold taken at $35 per ounce.

## COMPARATIVE COSTS

The erected cost of a four-compartment washing tray thickener is 25 per cent less than that of equivalent capacity in the form of a conventional C.C.D. plant, consisting of four single-compartment thickeners arranged in series.

Additional advantages of the washing tray thickener over the C.C.D. unit are 75 per cent less floor space required, 75 per cent less connected horsepower, one sludge pump instead of four, one foundation instead of four and much simpler control and sampling procedures.

The washing plants of the Cactus Mines Co. are in a warm climate and are installed entirely out of doors. Were these comparisons made in a northern area where the units would have to be installed in a building and possibly insulated against temperature drop, other advantages would be obtained. Not only would the 75 per cent reduction in floor area take on greater significance, but there might easily be a 50 to 60 per cent reduction in the building volume required and a 40 to 45 per cent reduction in exposed radiating surface.

## CONCLUSIONS

The data presented in this paper clearly show that when a washing tray thickener and a conventional C.C.D. unit are operated on an equal basis of feed, wash solution and volume, the former effects a 96.1 per cent recovery of the gold dissolved and the latter a 96.6 per cent recovery—a difference in favor of the C.C.D. unit of only 0.5 per cent.

## ACKNOWLEDGMENT

Acknowledgment is gratefully made to the management of the Cactus Mines Co. for permission to make these data available to the profession in the form of this technical paper. Acknowledgment is also made to several members of the author's company for assistance in arranging the material, especially A. M. Kivari of Los Angeles and Anthony Anable of New York.

# Milling Methods at New Cornelia

By L. M. Barker,* Member A.I.M.E.

(Tucson Meeting, November, 1938)

The New Cornelia Branch of the Phelps Dodge Corporation is at Ajo, Pima County, Ariz. It is at the southern terminus of the Tucson, Cornelia and Gila Bend Railroad, which connects with the Southern Pacific Railroad at Gila Bend, Ariz., approximately 43 miles to the north.

## History

Early history of the Ajo district has been related by A. W. Allen[1] and by T. A. Rickard.[2] Briefly, steps looking to the large-scale development of the ore body were instituted as early as 1912. This work culminated in the equipment of the property for open-pit mining by steam shovels. Ores initially mined carried economic amounts of copper carbonates as the principal copper-bearing mineral. Treatment methods developed for the extraction of the copper content involved leaching and a 5000-ton leaching plant was constructed and placed in operation in early 1917. Description of methods and equipment employed in this plant has been given by A. A. Tobelmann and James A. Potter.[3]

As exhaustion of the carbonate ore body neared, and mining operations exposed an adequate tonnage of sulphide ores, a 5000-ton concentrator was constructed for their treatment. That plant has been described by H. Kenyon Burch.[4] Construction was completed and the plant was placed in operation in early 1924. Changes made in the original plant to improve practices and increase production will be the subject of subsequent paragraphs of this paper.

## Geology

Description of the geology of the Ajo district has been published by Ira B. Joralemon[5] and by James Gilluly.[6] The ore occurs chiefly in the porphyritic facies of Cornelia quartz monzonite, though appreciable

---

Manuscript received at the office of the Institute Aug. 3, 1938. Issued as T.P. 1015 in Mining Technology, January, 1939.

* Concentrator Superintendent, New Cornelia Branch, Phelps Dodge Corporation, Ajo, Arizona.

[1] References are at the end of the paper.

bodies are found in diorite and rhyolite. The copper occurs principally as chalcopyrite, but bornite, chalcocite and native copper are present in notable amounts in certain areas. Copper minerals are finely disseminated both as discrete grains of small size and as narrow veinlets in the ore. Most of the ore is unusually hard, principally because of silicification of the monzonite. This characteristic, of course, introduces problems in both mining and milling.

## Mining and Milling

Mining is carried out by open-cut methods using electric shovels of 4½ yd. capacity. Shovels are served for disposal of ore and waste, by standard-gauge railroad transportation facilities.

The concentrator is on a hillside site about ¼ mile southeast of the town of Ajo and about 1 mile east of the mine. The site, although favorable for the mill proper, necessitated use of an extensive conveying system to connect it with the crushing plant. The choice of site was dictated by such considerations as: Accessibility to the mine haulage system and to the plant industrial track system; location with respect to the power house and other existing plant facilities; and relationship to tailings disposal sites.

The plant as originally constructed was designed to treat 5000 tons of ore per day. Additions and betterments made in the years which have intervened up to the present have accomplished increases in capacity until the present nominal rating is 20,000 tons of ore per day.

A brief outline of the more important changes made to effect this growth is offered in the accompanying chronological record of plant growth.

### *Chronological Record of Plant Growth*

| | |
|---|---|
| 1919–1920 | Pilot-plant operations. |
| 1924 | Original 5000-ton plant to operation. |
| 1928 | Original classifiers of 6-ft. width replaced by classifiers 8 ft. wide. |
| 1929 | Replaced No. 8 gyratories of intermediate crushing plant with 7-ft. standard cones. |
| | 6 by 12-ft. rod mills enlarged to 6 by 15 ft. (Dimensions inside linings.) |
| | McIntosh flotation cells substituted for Inspiration type Callows. |
| | Construction of three additional mill sections, a 275-ft. tailings thickener, a screening plant in fine-crushing department and additional surge-bin capacity in intermediate plant started. |
| 1930 | 1929 construction program completed and units turned to operation. |
| | Testing of merits of balls vs. rods as grinding media carried out. Also investigation of mill speeds. |
| | Regrinding of concentrates investigated. |
| 1931 | Testing of ball mills continued. |
| 1932 | Substitution of balls for rods as grinding media initiated. |
| | Plant down early 1932 to middle of 1934. |

| | |
|---|---|
| 1934 | Plant started. Replacement of rods by balls continued. |
| | Concentrate regrind unit installed. |
| 1935 | Speed of ball mills changed from 17 to 23.1 r.p.m. |
| | Testing of short-head cone started in fine-crushing plant. |
| 1936 | Hunt-Dunn flotation machines substituted for McIntosh. |
| | Additions made to fine-crushing screening plant and three short-head cones installed. |
| | Additional water storage installed. |
| 1937 | 78-in. rolls in fine-crushing plant replaced by short-head cones. |
| | 200-ft. tailings thickener installed. |
| | New tailings-disposal site prepared. |
| | 78-in. single spiral classifiers substituted for old classifying equipment. |
| | Additional filter-plant capacity installed. |

## COARSE CRUSHING

A flowsheet of the entire crushing plant is shown in Fig. 1, and details of equipment are given in the legend. Two coarse-crushing units are available. That involving the 48-in. gyratory was originally the coarse-crushing unit for the leaching plant. The 54-in. gyratory was installed solely for crushing sulphide ore. With the cessation of leaching operations, the 48-in. plant became available for the crushing of sulphide ores. Such adoption of units from the leaching plant was contemplated in the plans for treatment of sulphide ores. When milling at capacity, the 54-in. plant is operated three shifts per day and the 48-in. plant one to two shifts, depending on factors such as: the coarse-crushing burden imposed by the sizing of the run-of-mine ore; gyratory settings, and rate of ore delivery. Under average conditions the capacity of the 54-in. plant approximates 900 tons per hour and that of the 48-in. plant 600 tons per hour.

Ore is delivered to both crushers by trains of either five 30-yd. or six 20-yd. side-dumping cars. Maximum size of ore delivered from the mine is limited to that which will pass through the dipper opening of the 4½-yd. shovels. At the 54-in. crusher, cars are dumped into a 600-ton ore pocket surmounting an 8-ft. manganese-steel apron-type feeder, which delivers directly to the bowl of the 54-in. gyratory.

In the original installation the feeder discharged over a grizzly but maintenance on that device proved excessive and it was eliminated. Ore-delivery tracks extend over the gyratory bowl, so that dumping directly into the bowl is possible when occasion demands. At the 48-in. crusher all ore is dumped directly into the gyratory bowl. That procedure has the drawback that blocking of the crusher is a frequent occurrence when the ore is blocky.

Each gyratory is served by a suitable crane. At the 54-in. crusher the craneway extends over the apron conveyor and the dumping pocket. The cranes are essential, of course, in the handling of repair and renewal parts on the heavy equipment involved in these plants. They are also used extensively to clear the gyratories when the bowls become bridged by large boulders.

Both gyratories are operated with a setting ranging from 4 to 6 in. on the closed side. The smaller setting represents conditions when concaves and mantles are new and the larger setting results from normal wear of those elements. The product of the gyratories ranges, in its smallest dimension, from 6 to 8 in., dependent upon gyratory setting.

## INTERMEDIATE AND FINE CRUSHING

*Intermediate Crushing.*—Approximately 20,000 tons of live storage capacity is provided for coarse-crusher product at the intermediate crushing plant. This plant, in addition to ore-storage facilities, comprises four 7-ft. standard cones with the necessary apron feeders and conveyors to accomplish withdrawal of ore from storage and delivery to the cones. Cones are protected against tramp iron by large fixed magnets suspended over the ore stream at head pulleys of the conveyors feeding the cones. Bar grizzlies with 2-in. spacing remove undersize from the cone feed.

The cones are equipped with so-called "coarse-crushing" bowls and mantles. They are operated with a ⅝-in. setting on the closed side and yield a product minus 1 in. in size. Cone discharge and grizzly undersize combined constitute the final product of this crushing stage. Approximate screen analysis of this product is shown in the tabulation of screen analyses, Table 1.

Capacity of the intermediate plant is dependent upon the character of ores being treated, particularly as regards percentage of finished material in the feed. It is estimated that this varies from 15 to 30 per cent. Under average conditions this plant will handle 1300 tons per hour.

*Fine Crushing.*—The product of the intermediate plant is advanced by suitable conveyors to the fine-crushing plant. There it is delivered to a surge bin surmounting the screen installation. That installation consists of 48 screens, all electrically vibrated and representing several types of such devices. Screens are fed by drum-type feeders with gate control of feed ribbon. Usually a Ton-Cap screen cloth having 5⁄16 by ¾-in. openings is used, mounted with the longest dimension of the openings normal to the flow of ore. The screening plant is approximately 85 per cent efficient in effecting removal of undersize from screen feed. The undersize, screen analysis of which is given in Table 1, is routed by conveyors to mill storage bins, passing over a weightometer in transit. Screen oversize is conveyed to a surge bin and from that is delivered by means of apron feeders and conveyors to the short-head cones.

Six 7-ft. short-head cones comprise the fine-crushing devices. The first of these machines was installed for testing in 1935. As a result of that investigation two additional units were installed in 1936 to increase

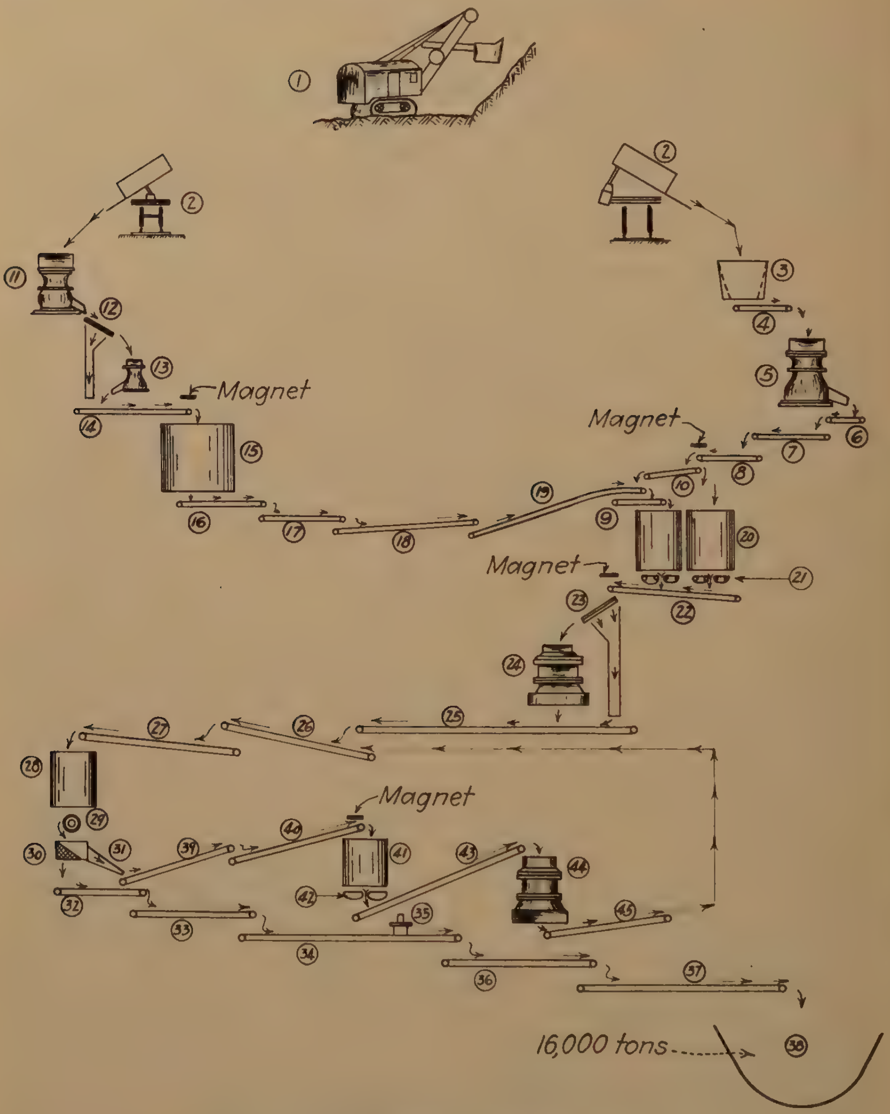


FIG. 1.—FLOWSHEET OF CRUSHING PLANT.

1. Full-revolving electric shovel, 4½-yd. dipper.
2. 20 and 30-yd. side-dumping cars, standard-gauge track.
3. One reinforced concrete hopper, 600 live tons.
4. One 8 ft. 0-in. manganese-steel apron feeder. 75-hp. motor, 575 r.p.m. Through gear and pinion reduction the feeder travels at 11 ft. per min. Length 72 ft. 0 in. Lift 19 ft. 0 in.
5. One 54-in. McCully crusher, driven by 300-hp. motor through belt drive to pinion.
6. One 5-ft. 0-in. manganese-steel apron feeder. 15-hp. motor, speed reducer, driving feeder at 30 ft. per min. Length 12 feet.
7. One No. 2 conveyor, 48-in. rubber belt, 662 ft. long, lift 79 ft. 0 in., speed 487 ft. per min. Driven by 100-hp. motor through gear and pinion reduction.
8. One No. 3 conveyor, 42-in. belt, 318 ft. long, 550 ft. per min. Driven by 50-hp. motor through gear and pinion reduction. Self-propelled and reversible tripper car. Conveyor over bin. Magnet at loading chute to 8.
9. One No. 3A conveyor, 42-in. belt, 314 ft. long, 450 ft. per min. Driven by 30-hp. motor through gear and pinion reduction. Self-propelled and reversible tripper car. Conveyor over bin.
10. One cross over conveyor, 42-in. belt, 116 ft. long, 390 ft. per min. Driven by 25-hp. motor through gear and pinion reduction.

*(For remainder of legend see opposite page.)*

fine-crushing capacity. Finally, in 1937 three sets of Ajo type 78-in. rolls were replaced by three short-heads to give a simplified, compact plant of desired capacity. Cones are operated with a 5⁄16-in. setting on the closed side, and with that setting can produce 1000 tons of finished material per hour. The cone discharges join the product of the intermediate plant for delivery to the screening plant, the cones thus being operated in closed circuit with the screens. By this practice a circulating load is built up so that actual tonnage of cone feed approximates 2.0 to 2.5 times tonnage finished. Typical screen analyses of feed and product are given in Table 1.

*General Data.*—The intermediate and fine-crushing plants are operated on afternoon and night shifts only. The operating time allotted is

---

11. One 48-in. gyratory crusher. Driven by 200-hp. motor through belt drive to pinion.
12. Four grizzlies. 70-lb. rails spaced 2-in. spaces.
13. Four No. 8 Gates gyratory crushers. Driven by 75-hp. motors through Texrope to pinion.
14. Two conveyors. No. 1A and 1B, 36-in. belt, 1130 ft. long, 290 ft. per min. Lift 51 ft. Driven by 75-hp. motor through speed reducer. Belt-propelled, clutch-type, tripper car. Over bin. Each conveyor has magnet.
15. One 15,000-ton steel ore bin. With manganese-steel gates on bottom to discharge into tripper cars.
16. Four conveyors, Nos. 2E, F, G, H., 24-in. belt, 225 ft. long, speed 450 ft. per min. Driven by 10-hp. motor through speed reducer. Self-propelled reversible tripper cars. Belt independent of tripper. Tripper feeds belt from floor of bin above.
17. One conveyor, No. C4, 48-in. belt, 415 ft. long, 450 ft. per minute. Driven by 100-hp. motor through gear and pinion reduction. Fed by 16.
18. One conveyor, No. C5, 48-in. belt, 418 ft. long, 440 ft. per min. Lift 46 ft. Fed by 17. Driven by 100-hp. motor through gear and pinion reduction.
19. One conveyor, No. C6, 48-in. belt, 480 ft. long, 440 ft. per min. Lift 54 ft. 0 in. Fed by 18. Driven by 100-hp. motor through gear and pinion reduction.
20. Two 7400-ton steel ore bins. Sliding gates feeding into apron feeders.
21. Four units of four 4-ft. 0-in. manganese-steel apron feeders. Driven from pulley on conveyor pulley through gear and pinion reduction. Speed 12 ft. per minute.
22. Four belts, No. 4, 36-in. belt. 170 ft. long, 272 ft. per min. 10-ft. lift. Driven by 10-hp. motor through gear and pinion reduction. Each belt has magnet over grizzlies.
23. Four grizzlies. Bars 2-in. spaces.
24. Four 7-ft. 0-in. standard cones. Driven by 300-hp., synchronous motors, direct connected.
25. Four conveyors. 28-in. belts, 355 ft. 0 in. long, 400 ft. per min. Lift 18 ft. 0 in. Driven by 20-hp. motor through speed reducer.
26. One conveyor, No. 5A, 60-in. belt, 632 ft. long, 650 ft. 0 in. per min. Lift 30 ft. 0 in. Driven by 200-hp. motor through speed reducer.
27. One conveyor, No. 5B, 60-in. belt, 717 ft. long, 650 ft. per min. Lift 26 ft. 0 in. Driven by 200-hp. motor through speed reducer. Self-propelled reversible tripper car over screen-feed bins.
28. One 750-ton steel bin for screen feed.
29. Forty-eight drum feeders to screens. 18-in. dia. and 46 in. long.
30. Forty-eight electric vibrating screens.
31. Twenty-four screen oversize-discharge chutes.
32. Two conveyors, No. 8A1, No. 8A2, 34-in. belts, 228 ft. 0 in. long, 440 ft. per min. Feed from screens. Driven by 25-hp. motor through gear and pinion reduction.
33. One conveyor, No. 8B, 42-in. belt, 158 ft. long, speed 420 ft. per min. Driven by 15-hp. motor through gear and pinion reduction.
34. One conveyor, No. 8, 42-in. belt, 521 ft. long, speed 470 ft. per minute. Lift 58 ft. 0 in. Driven by 100-hp. motor through gear and pinion reduction.
35. One weightometer.
36. One conveyor, No. 9, 48-in. belt, 820 ft. long, speed 490 ft. per min. Driven by 250-hp. motor through gear and pinion reduction. Lift 100 ft. 9 in.
37. One conveyor, No. 10, 42-in. belt, 1347 ft. long, speed 450 ft. per min. Driven by 100-hp. motor through gear and pinion reduction. Self-propelled reversible tripper car over 16,000-ton bin. Lift 39 ft. 0 in.
38. One 16,000-ton steel ore bin, suspended type.
39. One conveyor, No. 5C, 54-in. belt, 658 ft. 0 in. long, speed 570 ft. per min. Lift 30 ft. 0 in. Driven by 150-hp. motor through gear and pinion reduction.
40. One conveyor, No. 5D, 54-in. belt, 717 ft. 0 in. long, speed 570 ft. per min. Lift 26 ft. 0 in. Driven by 150-hp. motor through gear and pinion reduction. Self-propelled reversible tripper car. Has magnet before entering tripper car.
41. One 750-ton steel ore bin. Feeds 7-ft. short-head cones.
42. Six units, two per unit, 4-ft. 0-in. apron feeders. Manganese steel. Each unit driven by 15-hp motor through right-angled drive-speed reducer, thence through gear and pinion reduction.
43. Six conveyors, No. 6A, 26-in. belt, 80 ft. 0 in. long, speed 540 ft. per min. Driven direct by 10-hp. geared motor.
44. Six 7-ft. short-head cones. Driven by 250-hp. synchronous motors through pulleys and Texrope drive.
45. Six conveyors, No. 7, 28-in. belt, 150 ft. long, speed 480 ft. per min. Lift 16 ft. 0 in. Driven by 20-hp. motor through speed reducer.

adequate to permit production of 20,000 tons of mill feed of the sizing shown. The day shift is thus available for making essential repairs and replacements.

Both plants are equipped with cranes of ample capacity to handle any crusher part. Craneways extend into repair bays, where the cranes can be used to facilitate repair operations.

Each plant includes in its equipment an oil-circulation system involving a centrifuge for cleaning lubricating oil for the cones, and means of cooling the oil prior to its return to a gravity tank from which it is distributed to the individual cones. All cones are also equipped with the latest type of water seals, to prevent entry of dust into the lubrication system.

## Dust Control

Extensive facilities have been provided for dust control and additions are being made as investigation develops proper methods. Ore is sprayed with water at shovel locations in the mine prior to and during loading. At the crushing plant further wetting is accomplished during dumping and at numerous points in the crushing circuits. A low-pressure exhaust system (50,000 cu. ft. per min.) using wet collection methods serves the intermediate and fine-crushing plants. Conveyor loading points and transfer points are housed and connected to this system. In the screening plant screen feeders and screens are completely enclosed and exhausted. Screen feed bins and short-head feed bins have covers, which are automatically opened and closed by the tripper cars discharging to those bins. This device is a local development and its application to other bins is contemplated. A low-pressure system (10,000 cu. ft. per min.) is used to exhaust a group of conveyor junction points remote from the main plant and like systems are planned for other similar locations.

A great deal of attention has been given to cleaning conveyors, it having been found that dust carried on the return side of conveyors may be dispersed by the action of return idlers. A vacuum nozzle has been developed for application to this service. Vacuum cleaning apparatus is provided for removal of any dust accumulations on crushing-plant structures and the cleaning of these structures has been made a routine procedure.

## Power and Steel Consumption and Costs for Crushing

Power requirements of the entire crushing operation are distributed as shown in Table 2. Consumption of manganese steel in the crushing operation offers some criterion of the crushing duty. Distribution is shown in Table 2.

TABLE 1.—*Typical Screen Analyses of Crusher and Concentrator Products*

| Screen Size | Product of Standard Cone Crusher | Screen Feed | Screen Oversize | Product of Short-head Cone Crusher |
|---|---|---|---|---|
| Inch | | | | |
| +1.050 | 27.9 | 5.6 | 15.8 | |
| 0.742 | 15.6 | 4.2 | 9.1 | 1.3 |
| 0.525 | 14.8 | 7.9 | 14.1 | 6.4 |
| 0.371 | 9.5 | 17.8 | 29.7 | 23.3 |
| Mesh | | | | |
| 3 | 5.8 | 18.0 | 22.7 | 24.6 |
| 4 | 4.1 | 10.5 | 5.1 | 12.7 |
| −4 | 22.3 | 36.0 | 3.5 | 31.7 |
| | 100.0 | 100.0 | 100.0 | 100.0 |

| | Mill Feed | Primary Mill Discharge | Primary Classifier Sand | Secondary Mill Discharge | Secondary Classifier Sand | Flotation Feed |
|---|---|---|---|---|---|---|
| Mesh | | | | | | |
| + 4 | 25.6 | 2.6 | 2.8 | 0.2 | | |
| 6 | 17.7 | 2.0 | 1.6 | 0.2 | | |
| 8 | 8.9 | 2.0 | 1.4 | 0.2 | 0.2 | |
| 10 | 11.7 | 5.4 | 5.8 | 0.2 | 0.2 | |
| 14 | 6.2 | 5.4 | 6.6 | 0.4 | 0.6 | |
| 20 | 4.4 | 6.6 | 8.0 | 1.0 | 1.4 | |
| 28 | 4.4 | 10.2 | 13.2 | 3.8 | 4.8 | |
| 35 | 3.3 | 11.4 | 15.6 | 7.8 | 10.0 | |
| 48 | 2.8 | 11.2 | 15.6 | 15.6 | 20.2 | 1.3 |
| 65 | 2.4 | 10.0 | 12.6 | 23.2 | 28.6 | 6.0 |
| 100 | 2.5 | 8.0 | 7.2 | 16.4 | 16.8 | 14.2 |
| 150 | 2.1 | 5.2 | 3.0 | 9.2 | 7.6 | 13.3 |
| 200 | 1.3 | 2.6 | 1.2 | 4.2 | 3.0 | 9.9 |
| −200 | 6.7 | 17.4 | 5.4 | 17.6 | 6.6 | 55.3 |
| | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

| | General Mill Tails | Cleaner Tails | Final Concentrate |
|---|---|---|---|
| Mesh | | | |
| + 48 | 1.7 | | 0.3 |
| 65 | 6.3 | | 1.7 |
| 100 | 13.0 | 0.3 | 3.7 |
| 150 | 14.0 | 1.0 | 5.7 |
| 200 | 12.7 | 6.0 | 8.6 |
| −200 | 52.3 | 92.7 | 80.0 |
| | 100.0 | 100.0 | 100.0 |

Crushing costs for a recent month, representing curtailed operating conditions, are shown by departments and by elements in Table 3.

## Fine-ore Storage

The crushing-plant product is conveyed approximately 1200 ft. to the mill storage bins. Total lift of the conveying system approximates 200 ft. in that distance. The storage bin is of steel and of the suspended type. Its rated capacity is 16,000 tons, of which about 12,000 tons is live and readily discharged by gravity. It extends the length of the fine-grinding department.

Table 2.—*Power Requirements and Steel Consumption*

| Department | Kw-hr. per Ton Final Product |
|---|---|
| Coarse crushing | 0.16 |
| Standard cones | 0.56 |
| Short-head cones | 0.87 |
| Screens | 0.02 |
| Conveyors and magnets | 1.09 |
| Dust collection | 0.05 |
| Lighting | 0.04 |
| Total crushing | 2.79 |

| Department | Approximate Yearly Consumption of Steel, Lb. |
|---|---|
| Coarse crushing: apron feeder links, concaves, mantles, liners, etc. | 103,350 |
| Intermediate crushing: grizzly bars, standard cones, chute liners, etc. | 155,650 |
| Fine crushing: cones, chute liners, etc | 226,650 |
| Total | 485,650 |
| Pounds per ton ore milled | 0.081 |

Table 3.—*Crushing Costs per Ton Mill Feed*

| Department | Operation | Repairs | Total |
|---|---|---|---|
| Coarse crushing | $0.007 | $0.014 | $0.021 |
| Standard cones | 0.005 | 0.008 | 0.013 |
| Short-head cones | 0.012 | 0.012 | 0.024 |
| Conveying | 0.015 | 0.012 | 0.027 |
| Screens | 0.001 | 0.002 | 0.003 |
| Totals | $0.040 | $0.048 | $0.088 |

| Element | |
|---|---|
| Labor | $0.034 |
| Supplies | 0.035 |
| Power | 0.015 |
| Miscellaneous | 0.004 |
| Total | $0.088 |

## Fine Grinding

The fine-grinding department is divided into eight units or sections. A flowsheet of a typical section is given in Fig. 2 and the accompanying legend gives details of equipment. These units each have a nominal rating of 2500 tons per day when grinding to minus 48 mesh. A modified two-stage grinding practice is followed, in that a portion of the sands of the primary classifiers is diverted to feed the secondary mills. Both primary and secondary classifiers produce finished overflows. In the past various grinding flowsheets were tried but nothing was developed that would warrant the reconstruction expense involved in effecting a change. This grinding flow offers the following advantages: Primary ore slimes are removed from the grinding circuit under conditions that permit maximum pulp density for a given grind; the relatively clean sand fed to the secondary grinding circuit necessitates a high pulp density in secondary classifier overflows; ball-mill feed sizing in each grinding stage permits rationing of ball sizes to suit respective feeds.

Ball mills are of the displacement type and measure approximately 6 by 15 ft. inside the liners. They operate at 23.1 r.p.m., which is approximately 75 per cent of the critical speed. Ball loads average about 28 tons of cast semisteel balls. Make-up to the primary mills consists of 3-in. balls and to the secondary mills of 2½-in. balls. The question of ball size and screen analysis of ball charges is the subject of current research. Evidence has been accumulated, which indicates that ball charges in both grinding stages involve too great a proportion of large balls for proper rationing of ball sizes to feed sizes. Whether theoretical conditions can be achieved remains to be determined. If such conditions can be obtained, a considerable experience will be necessary to determine their practicability.

Breast linings of ball mills consist of interlocking sawed rail sections set with the rail axis normal to the mill shell and grouted in place. Approximately 19 tons of steel is required for such a lining. End liners are of cast semisteel and are bolted in place. The feed-end liner consists of two parts with a total weight of 5450 lb. and the discharge liner is a one-piece casting weighing 4400 lb. For lining, mills are removed from stands and transferred to a repair bay by a 60-ton crane. Ends are removed, the ball charge is dumped and remnants of the old lining are broken out. Placing of a new lining requires three days and about nine man-shifts of labor. This type of lining, though offering certain advantages, is not all that could be desired. At present, several other types of linings are being tested with a view to the ultimate improvement of lining practice.

Classification has received a great deal of attention during the history of this operation. The installation of single spiral classifiers made in 1937 had as its purpose an increase in circulating loads in grinding circuits for a resultant gain in capacity. Circulation, as percentage of new feed, now approaches 200 per cent in primary mills and 500 per cent in secondaries. Much remains to be done to improve classification efficiency, but it is believed solution to that problem will follow as a result of improvement in grinding practices. Screen analyses of grinding-circuit products are given in Table 1.

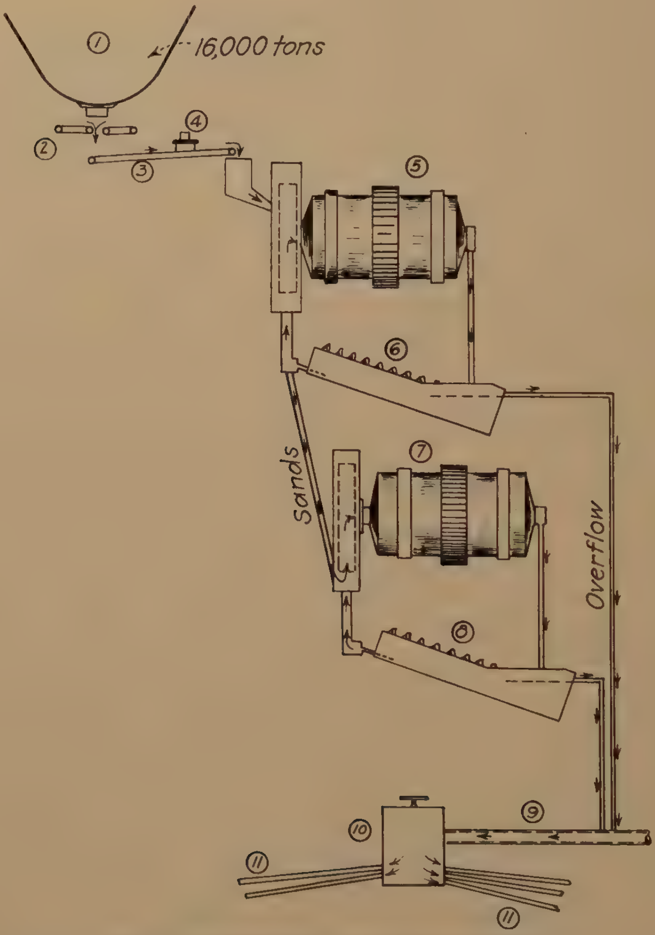


Fig. 2.—Flowsheet of grinding circuit.

1. One 16,000-ton mill ore bin. Suspended type.
2. Sixteen feeders, conveyor. 42-in. belts, 54 ft. long, speed 32 ft. per min. Driven by 2-hp. motor through reducer.
3. Eight conveyors, No. 11, 24-in. belt, 92 ft. long, speed 150 ft. per min., lift 9 ft. 0 in. Driven by 5-hp. motor through gear and pinion reduction.
4. Eight weightometers.
5. Sixteen 6 by 15-ft. primary ball mills. Driven by 300-hp. synchronous motors. Magnetic clutch. Speed of mills, 23.1 r.p.m. Two mills per unit.
6. Sixteen 78-in. single spiral classifiers. Driven at 3½ r.p.m. by 7½-hp. MotoReducers.
7. Sixteen 6 by 15-ft. secondary ball mills. Driven by 300-hp. synchronous motors. Magnetic clutch. Speed of mills, 23.1 r.p.m. Two mills per unit.
8. Sixteen 78-in. single spiral classifiers. Driven at 3½ r.p.m. by 7½-hp. MotoReducers.
9. Eight main 12-in. headers, from primary and secondary classifier overflow. One mill per unit.
10. Two pulp distributors to flotation machines.
11. Ten launders; five launders from each pulp distributor to flotation machines.

Power requirements approximate the figures in Table 4. Consumption of balls and liners is shown also in that table.

TABLE 4.—*Power Requirements and Consumption of Balls and Liners*

| Power | Kw-hr | Steel | Lb. per Ton Milled |
|---|---|---|---|
| Per ton ore milled | 7.58 | Balls | 1.940 |
| Per ton — 65-mesh produced | 9.64 | Liners | 0.157 |
| Per ton — 200-mesh produced | 17.07 | | |
| | | Total | 2.097 |

## FLOTATION

The flowsheet of the flotation operation is shown in Fig. 3. For rougher flotation the plant is divided into two units. The classifier overflows of four grinding units are combined in a pulp distributor serving each of these units. The distributors apportion the pulp among five 62-ft. Hunt-Dunn cells. These cells are of the double spitzkasten type and are equipped with submerged air ports of self-sealing type. Control of air volume is afforded by gate valves on the branch air line serving each cell and also by two slide valves, one controlling air ports in the first 20 ft. of the cell and another the air ports of the last 20 ft. Each cell has a capacity of 2000 tons of ore per day at a pulp density of 20 to 24 per cent solids.

Inasmuch as regrinding of rougher concentrates is practiced, maximum flotation of middling particles is desired in the rougher flotation. Accordingly, all rougher froth produced is passed to re-treatment. This practice tends to lower the ratio of concentration of the roughing step but benefits recovery. Copper content of rougher concentrate varies from 16 to 25 per cent, iron content from 11 to 21 per cent, and insoluble content from 32 to 50 per cent, dependent upon type of ores being treated. Ratio of concentration varies from 16 to 25 into 1.

In concentrate re-treatment, rougher concentrates are first treated in a 12-ft. Hunt type of cell, which recovers the greater part of the free mineral present in the rougher concentrate as a finished concentrate. This constitutes from 50 to 75 per cent of the total tonnage of final concentrates. Tailings from this cell are then classified and reground as indicated in the flowsheet. The use of this cleaning cell in the flowsheet is given special mention because it accomplishes removal of coarse free mineral from the system, thus minimizing the burden on the regrind unit and eliminating the overgrinding of such minerals, which would normally occur. The product of the regrinding unit demands two-stage cleaning to produce a final concentrate. In all cleaning steps washing of the froth by fresh-water sprays has been found to be helpful in reducing insoluble content of concentrates.

Flotation reagents generally employed are: lime, American Cyanamid reagent No. 244, and G. N. S. No. 5 pine oil. The lime is fed as milk

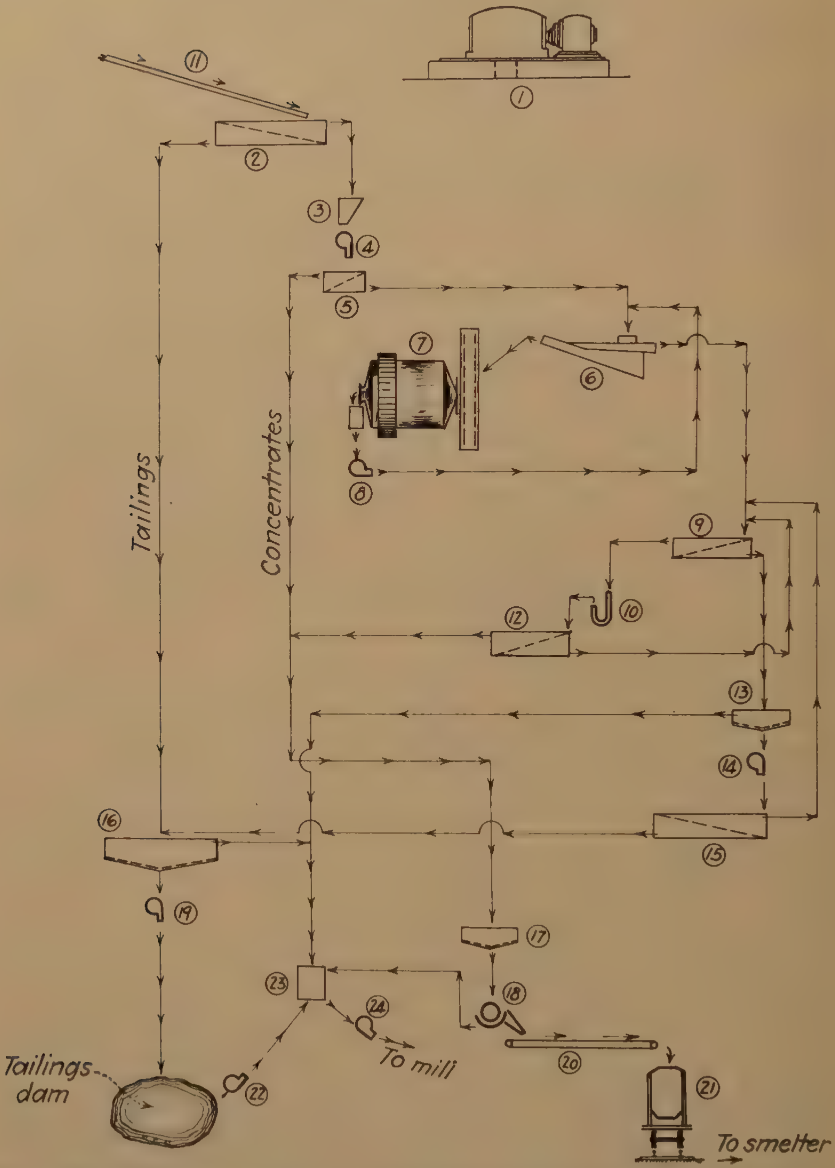


FIG. 3.—FLOWSHEET OF FLOTATION, CONCENTRATE HANDLING AND TAILINGS DISPOSAL.

1. (Air production. All air at 2-lb. pressure.)

Two 20,000-cu. ft. per min. centrifugal blowers. Driven direct by 650-hp. synchronous motors at 3600 r.p.m.

One 30,000-cu. ft. per min. centrifugal blower. Driven direct by 650-hp. synchronous motor at 3600 r.p.m.

Two No. 8 cycloidal blowers, 8000 cu. ft. per min. each. Driven by 200-hp. motors through belt and pulleys.

2. Ten 62-ft. 0-in. Hunt-Dunn type flotation machines.
3. One sump.
4. Two 6-in. sand pumps.
5. One 12-ft. Hunt type re-treatment cell.
6. Three 13 ft. 0-in. bowl-type classifiers. Speed bowl rakes 6 r.p.m. Sand rakes 18 s.p.m.

*(For remainder of legend see opposite page.)*

to both the primary and secondary grinding circuits. The collector is fed by chain-bucket type feeders to the overflows of primary classifiers. Pine oil is added at the same point, control being by needle valves. Xanthates are used as collectors on ores carrying native copper and cuprite. Xanthate is also used in the scavenger treatment of cleaner tailings.

Flotation air is provided by one 30,000 and two 20,000-cu. ft. per min. centrifugal compressors delivering air at 2-lb. pressure. This represents approximately 6000 cu. ft. per min. per operating cell in the plant. Two No. 8 cycloidal blowers are available as spares.

## CONCENTRATE HANDLING AND TAILINGS DISPOSAL

Handling concentrate presents no unusual features. With the adoption of the primary cleaner cell described under Flotation, a marked increase in filter capacity was obtained and the moisture content of filter cake was reduced from approximately 9.5 to 7.5 per cent.

To minimize fresh-water consumption and reduce pumping costs on return water, tailings are thickened before disposal. One 275-ft. and two 200-ft. traction thickeners are available for this service. Feed to thickeners has a density of approximately 20 per cent solids and discharges carry approximately 45 per cent solids. Water recovered by thickening is laundered to a pumping station at the filter plant and returned to the mill-water system.

Thickener discharges are piped and laundered to an installation of 8-in. sand pumps. Pumping of tailings is necessitated by the relationship of tailings-disposal sites to the mill site and by the need for so conducting tailings disposal that water may be reclaimed. The pumps deliver to two 15-in. wood-stave lines, each of which extends around approximately one-half the periphery of the tailings pond. These lines are mounted horizontally on trestles a suitable distance inside pond limits. Tailings are spigoted from the lines through 4-in. nozzles toward a berm erected at the pond border. Deposition of the coarser tailings close to the berm is thus accomplished. As filling of the pond border with coarse tailings progresses, the berm is built up to a new level by the use of a dragline

---

7. One 8 by 12-ft. ball mill. Regrind, 12 r.p.m. Driven by 300-hp. synchronous motor.
8. Two 6-in. sand pumps.
9. One 38-ft. 0-in. Hunt-Dunn type flotation cell.
10. One air lift, 25-lb. pressure.
11. Ten flotation launders from pulp distributors.
12. One 21-ft. Hunt-Dunn type flotation cell.
13. Two 60-ft. thickeners.
14. Two 6-in. sand pumps.
15. One 62-ft. 0-in. Hunt-Dunn scavenger flotation cell.
16. One 275-ft. slime traction thickener. Two 200-ft. slime traction thickeners.
17. Two 60-ft. thickeners.
18. Four 14 by 14-ft. drum-type filters. Two 8-ft. 6-in. 7-disk filters.
19. Four 8-in. sand pumps.
20. One conveyor, No. 12, 24-in. belt, 744 ft. long, belt speed 110 ft. per min. Drop 11 ft. 0 in. Driven by 7½-hp. motor through reducer.
21. 60-ton concentrate cars to smelter.
22. Two 5000-gal. per min. fresh-water pumps. Direct driven by 250-hp. induction motor.
23. One reservoir, receiving all reclaimed water.
24. Five return-water pumps: two 5000 gal. per min.; three 3000 gal. per minute.

powered by a gasoline motor. Tailings slimes and water gravitate toward the pond center, where slimes settle and water is reclaimed as described below.

Two tailings-disposal sites are in use at present, each comprising an area of approximately 200 acres. Besides tailings-disposal facilities the sites include water-reclaiming towers centrally located in each area and connected by suitable pipe lines to pump stations beyond the pond limits. Pumps at these stations deliver reclaimed water to the mill system.

## WATER

The fresh-water supply for the mill is obtained from wells in a valley approximately seven miles from the mill site. An extensive pumping plant is installed there at a station 700 ft. underground. Detailed description of that installation will not be undertaken in this paper. Well pumps deliver water through a 20-in. steel pipe line to the mill reservoirs. Another 10-in. line is provided for the handling of domestic water. The total lift involved from well to mill approximates 1160 ft. Two interconnected reservoirs at the mill site provide approximately 6,500,000 gal. of storage capacity.

Water requirements for milling approximate 1000 gal. per ton of ore milled. Distribution of this water as to source is as follows: tailings and concentrate thickening, 640 gal. per ton milled; tailings ponds, 160; well (fresh water), 200.

## POWER REQUIREMENTS OF MILL

Power consumption by divisions of the mill proper when milling at capacity is distributed as follows:

| Division | Kw-hr. per Ton Milled | Division | Kw-hr. per Ton Milled |
|---|---|---|---|
| Fine grinding | 7.58 | Reclaimed water | 0.89 |
| Flotation | 1.42 | Concentrate regrinding | 0.44 |
| Concentrate handling | 0.12 | Lighting | 0.07 |
| Tailings disposal | 0.28 | Miscellaneous | 0.06 |
| | | Total | 10.86 |

## METALLURGICAL CONTROL

Ore is weighed by weightometer as it is delivered to the fine-ore storage. A hand sample of the ore stream is taken for moisture determination. Tonnage fed to each fine-grinding unit is also determined by weightometer and a hand sample is again taken for moisture determination. Frequent checking of weightometers suffices to maintain close agreement between tonnage weighed into and out of fine storage.

Sampling methods used involve both hand sampling and autosampling. Feed to each mill unit is sampled by hand at 15-min. intervals. Unit feed samples are then composited to give a general heading sample for each operating shift. Although automatic sampling would be desirable, the distribution of metal content of the ore makes hand sampling reliable. All special sampling is by hand. General mill tailings and concentrates are sampled by shifts by autosamplers operating at 15-min. intervals. Filtered concentrates are hand-sampled as they are loaded into cars. This sample is for mill control only, the smelter control sample being taken at the smelter. Weight of concentrates shipped is obtained by railroad scales.

The extent to which fine grinding is carried for rougher flotation is dictated by considerations such as degree of dissemination of copper minerals in the ore being treated, density of pulp resulting from a given grind, and influence of degree of grind on mill capacity. The percentage of plus 65-mesh material in the flotation feed is used as the grinding criterion. Although, in general, New Cornelia ores, particularly those carrying chalcopyrite, do not demand extremely fine grinding for rougher flotation separation, certain middling particles are floated that demand minus 200-mesh grinding to effect liberation of sulphides. An initial grind of 8 to 10 per cent plus 65-mesh is maintained on such ores. Chalcocite ores present in the mine show unusual dissemination of the chalcocite and thus demand finer grinding. It has been found desirable to grind to 6 per cent plus 65-mesh when such ore is present in the mill feed. The tailing screen analyses in Table 5, showing copper distribution, exemplify the grinding problem.

TABLE 5.—*Tailing Screen Analyses*

| Mesh | Ore Carrying | | | |
|---|---|---|---|---|
| | Chalcopyrite | | Chalcocite | |
| | Material, Per Cent | Cu, Per Cent | Material, Per Cent | Cu, Per Cent |
| On 65 | 8.7 | 0.160 | 6.0 | 0.280 |
| 100 | 13.3 | 0.075 | 13.3 | 0.115 |
| 150 | 14.7 | 0.055 | 15.7 | 0.090 |
| 200 | 11.7 | 0.045 | 12.7 | 0.070 |
| Through 200 | 51.6 | 0.060 | 52.3 | 0.090 |
| Original | | 0.070 | | 0.100 |

The importance of grind in relation to the grade of final concentrates produced is reflected by the screen analysis of a monthly concentrate composite (Table 6).

TABLE 6.—*Screen Analysis of Monthly Concentrate Composite*

| Mesh | Material, Per Cent | Cu, Per Cent | Insol., Per Cent | Fe, Per Cent |
|---|---|---|---|---|
| On 65 | 2.0 | 18.90 | 33.8 | 20.5 |
| 100 | 3.7 | 22.31 | 27.9 | 21.6 |
| 150 | 5.7 | 26.18 | 23.0 | 22.8 |
| 200 | 8.6 | 26.09 | 22.0 | 22.9 |
| Through 200 | 80.0 | 32.87 | 8.8 | 25.7 |
| Original |  | 31.04 | 12.2 | 24.5 |

TABLE 7.—*One Month's Record*

| | | | |
|---|---|---|---|
| Dry tons ore milled | 356,800[a] | Mill feed, percentage of plus 4-mesh | 26.2 |
| Dry tons ore milled per day | 13,723 | Flotation feed, percentage of plus 65-mesh | 8.2 |
| Operating days | 26 | Flotation feed, percentage of solids | 22.6 |
| Running time, percentage of total | 99.30 | Tailings to dam, percentage of solids | 41.5 |
| Dry tons concentrates produced | 10,240 | Filter cake, moisture, per cent | 6.52 |
| Ratio of concentration, tons into one | 34.84 | | |

| | | | Total Shifts | Tons per Shift |
|---|---|---|---|---|
| Feed: | | Labor: | | |
| Total Cu, per cent | 0.97 | Crushing | 1587 | 224.8 |
| Oxide Cu, per cent | 0.01 | Mill operating | 2431 | 146.8 |
| Silver, oz. per ton | 0.074 | Mechanical | 2815 | 126.7 |
| Gold, oz. per ton | 0.0057 | | | |
| Tailing: | | Total | 6833 | 52.2 |
| Total Cu, per cent | 0.08 | Power, kw-hr. per ton: | | |
| Oxide Cu, per cent | 0.01 | Crushing | | 2.80 |
| Concentrate: | | Milling | | 11.29 |
| Cu, per cent | 31.16 | | | |
| Silver, oz. per ton | 2.190 | Total | | 14.09 |
| Gold, oz. per ton | 0.160 | Reagents, lb. per ton ore | | |
| Insoluble, per cent | 12.1 | Pine oil | | 0.167 |
| Iron, per cent | 24.7 | Reagent No. 244 | | 0.025 |
| Indicated extractions, percentage: | | Lime | | 1.05 |
| | | Fresh water, gal. per ton | | 245 |
| Total Cu | 92.46 | | | |
| Sulphide Cu | 93.40 | | | |
| Silver | 84.55 | | | |
| Gold | 80.34 | | | |

---

[a] Curtailed operating conditions.

In the flotation operation regulation of pulp alkalinity and of collector and frother types and quantities is important. A variety of ore types are represented in the mine and they are not uniform in their response to flotation treatment. This condition is reflected in abrupt changes of ore in mill circuits and, because of the direct connection between fine grinding and flotation, changes in flotation conditions are pronounced. Such changes are, in the main, met by changes in pulp alkalinity, but changes in collector and frother are occasionally necessary. Pulp alkalinity is determined hourly, as a routine procedure, by titration with a standard acid solution. More frequent determinations are made when need for them is indicated. Alkalinity is reported in terms of grains of excess CaO per gallon of water and is varied from 2.0 to as high as 8.0 grains, dependent upon the factors mentioned.

## METALLURGICAL AND OPERATING DATA

In Table 7 significant data are presented for a recent month.

## MILLING COSTS, INCLUDING CRUSHING

Milling costs for a recent month under curtailed operating conditions are shown by departments and by elements in Table 8.

TABLE 8.—*Milling Costs*

| Department | Per Ton Mill Feed | Elements | Per Ton Mill Feed |
|---|---|---|---|
| Crushing | $0.088 | Labor | $0.088 |
| Fine grinding | 0.098 | Supplies | 0.116 |
| Flotation | 0.042 | Power | 0.074 |
| Concentrate re-treatment | 0.006 | Fresh water | 0.013 |
| Concentrate handling | 0.009 | Miscellaneous | 0.017 |
| Tailings disposal | 0.013 | | |
| Mill water | 0.029 | Total | $0.308 |
| Miscellaneous | 0.023 | | |
| Total | $0.308 | | |

## MISCELLANEOUS

Power for milling operations is furnished by the power plant constructed to serve initial operations at the property. In that plant steam is generated by gas-fired boilers and electrical energy by turbines. Power is delivered at 2300 volts by transmission lines to substations at the crushing plant and mill. At these stations is installed switching equipment for distribution of the 2300-volt power and transformers for production of 440-volt and 110-volt power. In general, all motors of 25 hp. and above used in the mill are 2300 volts and smaller ones 440 volts.

The extensive use of synchronous motors in the crushing plant and mill results in the maintenance of a high power factor on the total power-plant load.

The following maintenance departments are provided at the mill; a carpenter shop, machine shop, paint shop and pipe shop. Services of the various general plant shops are also available for construction or repair jobs that cannot be handled by mill facilities. The general plant shops include a completely equipped machine shop, a boiler shop and an electric shop.

Supplies of all types are obtained through the Branch Supply Department, which maintains adequate stocks in a warehouse within the plant grounds.

Analytical work and preparation of mill samples are done by the local assay office which serves both mine and mill under the supervision of a chief chemist.

## Safety

Safety has received unremitting attention in this operation. All phases of a comprehensive program involving employee education, first-aid training, development of safe practices and safeguarding of equipment are being actively prosecuted.

## Acknowledgment

The author extends his thanks to the management of Phelps Dodge Corporation for permission to publish this description of one phase of the operations of the New Cornelia Branch.

## References

1. A. W. Allen: Ajo Enterprise of the New Cornelia Copper Company. *Eng. and Min. Jnl.* (1922) **113, 114.**
2. T. A. Rickard: The Later Story of the New Cornelia Enterprise. *Eng. and Min. Jnl.* (1925) **119.**
3. A. A. Tobelmann and James A. Potter: First Year of Leaching by New Cornelia Copper Company. *Trans.* A.I.M.E. (1919) **60,** 22.
4. K. K. Burch: New Cornelia Concentrating Mill at Ajo, Arizona. *Eng. and Min. Jnl.* (1924) **118.**
5. I. B. Joralemon: The Ajo Copper Mining District. *Trans.* A.I.M.E. (1914) **49,** 593.
6. J. Gilluly: Geology and Ore Deposits of the Ajo Quadrangle, Arizona. Arizona Bur. Mines Geol. Ser. No. 9, *Bull.* 141.

# INDEX

(NOTE: In this index the names of authors of papers and discussions and of men referred to are printed in SMALL CAPITALS and the title of papers in *italics*.)

A

Achotla chloridizing mill, 243
Adsorption: cause, 27
  meaning, 26
ALLEN, H. P.: *The Achotla Chloridizing Mill*, 243
Allis-Chalmers Mfg. Co.: tests of grindability of various ores, 296
Amalgamation: electrical: explanation, 265
  electrocapillary: conditions suitable for, 271
    definition, 265
    effect of electrocapillary phenomenon on amalgamation, 267
    electrocapillary phenomenon, 266
    explanation of action, 270
Anglesite: flotation: influence of sodium sulphide, alkalies and copper sulphate on effect of xanthate at mineral surfaces, 10, 18
Arsenopyrite: flotation: temperature influence, 41
Attrition milling: conditioning surfaces of minerals for flotation: nonmetallic minerals, 65

B

Ball mills: efficiency compared with drop weight, 291
BARKER, L. M.: *Milling Methods at New Cornelia*, 434
BELL, G. A.: *Milling Practice at Demonstration Gold Mines, Ltd., Philippine Islands*, 236
BENEDICT, C. H.: *Discussions: on Grindability and Grinding Characteristics of Ores*, 321
  *65-mesh Grinding in Closed Circuit with Stainless-steel Screens*, 368
Benguet Consolidated Mining Co.: milling developments, 224
BIRD, B. M.: *Discussion on Principles of Flotation*, 40
BOND, F. C. AND MAXSON, W. L.: *Grindability and Grinding Characteristics of Ores*, 296; *discussion*, 323

C

Cactus mines mill: flowsheet, 427
  washing tray thickener versus countercurrent decantation plant, 426
Carbon: flotation: 190, 201, 206
Cement: grinding raw materials: closed-circuit:
      chemical control, 354
      Leeds, Ala., 344
    mesh of grind, 352, 359
Cement: grinding raw materials: closed circuit:
      mill speed, 359
    power requirements, 351
    slurry moisture: control, 355
Cement clinker: grindability tests, 313
Cerussite: flotation: influence of sodium sulphide, alkalies and copper sulphate on effect of xanthate at mineral surfaces, 10, 18
Chalcopyrite: flotation: temperature influence, 41
CHAPMAN, T. G.: *A Cyanide Process Based on the Simultaneous Dissolution and Adsorption of Gold*, 207; *discussion*, 221
Charcoal: activated: preparation for use in process of simultaneous dissolution of gold in cyanide and adsorption on charcoal, 221
  flotation: with adsorbed gold, 216
  sugar: ash-free: flotation, 201, 206
Chloridization: gold-silver ores: Achotla mill, Mexico, 243
  Holt-Dern process, 244
Classification. *See* Grinding and Classification.
Coal: anthracite: flotation: oil-air separation, 190
  bituminous: flotation: oil-air separation, 190
Coal washing: flocculation and clarification of slurry: age of reagent: effect on flocculating properties, 161
    bibliography, 164
    causticized starch as reagent, 157
    flocculating agents, 152
    starch reagents, 152
Coercimeter: construction, 283
  definition, 282
  use in grinding tests, 282
COGHILL, W. H.: *Discussion on the "Electric Ear," a Device for Automatically Controlling the Operation of Grinding Mills by Their Sound*, 388
COGHILL, W. H. AND DE VANEY, F. D.: *Use of the Coercimeter in Grinding Tests*, 282
Coke: petroleum. *See* Petroleum Coke.
Columbia University: study of: oil-air separation of nonsulphide and nonmetal minerals, 180
Cooley roasting furnace, 392
Copper milling: flotation: New Cornelia, 445
  New Cornelia: costs, 440, 451
    crushing: coarse, 436
      costs, 440
      intermediate and fine, 437
      power requirements, 440
      steel consumption, 440

Copper milling: New Cornelia: dust control, 440
    flotation, 445
    grinding: fine, 442
    metallurgical control, 448
    power requirements, 440, 448
    tailing: screen analyses, 449
    tailings disposal, 447
Copper ore (*see also* Sulphide Minerals):
  grindability tests, 311
Counselman, T. B.: *Closed-circuit Grinding of Cement Raw Materials at Leeds*, 344; *discussion*, 359
  *Discussions: on the "Electric Ear," a Device for Automatically Controlling the Operation of Grinding Mills by Their Sound*, 388
    *on Grindability and Grinding Characteristics of Ores*, 317 et seq.
    *on 65-mesh Grinding in Closed Circuit with Stainless-steel Screens*, 366 et seq.
Cox, A. B. and Wark, I. W.: *Principles of Flotation*, IV—*An Experimental Study of Influence of Sodium Sulfide, Alkalies and Copper Sulfate on Effect of Xanthates at Mineral Surfaces*, 7
  *Principles of Flotation*, V—*Conception of Adsorption Applied to Flotation Reagents*, 26
  *Principles of Flotation*, VI—*Influence of Temperature on Effect of Copper Sulphate, Alkalies and Sodium Cyanide on Adsorption of Xanthates at Mineral Surfaces*, 41; *discussion*, 52
  *Discussion on Oil-air Separation of Nonsulphide and Nonmetal Minerals*, 199
Craig, J. J.: *Discussion on First Magnetic Roasting Plant in Lake Superior Region*, 406
Crockett, R. E.: *Discussion on First Magnetic Roasting Plant in Lake Superior Region*, 406
Crushing and grinding: pendulum impact tests for measuring surface energy of ore, 307, 317
  screen analyses: calculating surface and other properties, 300
    correcting, 300, 317
Cyanidation: Benguet gold mines, 224
  flocculation of slime with starch solutions: experiments, 168
  gold: simultaneous dissolution by cyanide and adsorption on activated charcoal, 207
  oxide ores: Demonstration Gold Mines, P.I., 236
  preceded by chloridizing: Achotla mill, Mexico, 243
  washing efficiencies: washing tray thickener versus conventional countercurrent decantation plant, 424

D

Davis, C. W.: *Discussion on Mineralogical Characteristics Affecting the Concentration of a Semioxidized Lead-silver Ore*, 178
Davis, E. W.: *First Magnetic Roasting Plant in the Lake Superior Region*, 389; *discussion*, 408
  *Discussions: on Grindability and Grinding Characteristics of Ores*, 320, 321, 322
    *on Use of the Coercimeter in Grinding Tests*, 295
Dean, R. S.: *Magnetite as a Standard Material for Measuring Grinding Efficiency*, 324
  *Discussion on Principles of Flotation*, 39
Dean, R. S. and Hersberger, A. B.: *New Flotation Reagents*, 81
del Giudice, G. R. M., Taggart, A. F., Sadler, A. M. and Hassialis, M.: *Oil-air Separation of Nonsulphide and Nonmetal Minerals*, 180
Demonstration Gold Mines, P.I., milling practice, 236
DeVaney, F. D. and Coghill, W. H.: *Use of the Coercimeter in Grinding Tests*, 282
Dorr Company, Inc.: flowsheet for grinding cement raw materials, 345
  licensor cyanide process based on simultaneous dissolution and adsorption of gold, 207
  modern trends in classification, 274
  washing tray thickener, 424
Drop weight: grinding efficiency compared with ball mill, 291

E

Eames, L. B.: *Discussion on A Cyanide Process Based on the Simultaneous Dissolution and Adsorption of Gold*, 223
Eggleston, G. C., Keck, W. E. and Lowry, W. W.: *A Study of the Flotative Properties of Hematite*, 102
Electric Ear: automatic control of operation of grinding mills by their sound, 371
Electrostatic separation: selective: classification of minerals as reversible negative and reversible positive, 415, 420
    interchange of polarity of electrodes: effect on separation, 413
    reversibility of minerals, 413
    study of electrostatic conductivity, 409
    sticking to rotor beneficial or not? 421
Emulsol. *See* Flotation Reagents.
Eye, C. M.: *Discussion on Milling Developments at the Benguet Consolidated Plant*, 234

F

Flocculation of slimes: brief bibliography, 164
  with starch solutions: patents deter would-be users, 168
    process, 146
Flotagen: flotation agent: influence of alkalies, cyanide and copper sulphate on adsorption by galena, sphalerite, pyrite and chalcopyrite, 53
Flotation (*see also* names of minerals):
  adsorption: cause, 27
    meaning of term, 26

Flotation: air levitation principles for nonsulphide nonmetal minerals same as for sulphides and native metals, 180
  charcoal with adsorbed gold, 216
  froth: conditioning surfaces for: chemical treatment: nonmetallic minerals, 65
      attrition milling: nonmetallic minerals, 65
      laboratory study, 65
  levitation: definition, 180
  Murex process, 87
  oil-air separation: classification of nonsulphide nonmetal minerals: nonsiliceous oxidized minerals of alkalies and alkaline earths, 181
      oxidized metalliferous minerals, 181
      salt mush, 198
      siliceous minerals, 181
      sulphur and carbonaceous solids, 181
    effect of slime in pulp, 196
    principles, 181
    solution-oiling theory, 197, 198
  principles: adsorption theory, 26
    chemical theory, 28
    chemical theory versus adsorption theory, 26, 191, 199, 204
    conception of adsorption applied to flotation reagents, 26
    influence of sodium sulphide, alkalies and copper sulphate on effect of xanthates at mineral surfaces: experimental study, 7
      interpretation, in terms of chemical theory, 24
    mercaptobenzthiazole as agent: influence of alkalies, cyanide and copper sulphate on adsorption by galena, sphalerite, pyrite and chalcopyrite, 53
    oil-air separation, 181
    temperature influence on effect of copper sulphate, alkalies and sodium cyanide on adsorption of xanthates at mineral surfaces, 41
    xanthates: effect at mineral surfaces influenced by sodium sulphide, alkalies and copper sulphate, 7
      loss in solutions in contact with sulphur, 185
Flotation reagents: collectors: for use with Emulsol (X-1), 87
  effects attributed to adsorption, 26
  Emulsol (X-1): laboratory tests, 81
  frothing: Emulsol (X-1), 84
    ideal, 83
  long-carbon-chain organic compounds with lypophile hydrophile unbalance, 81
  mercaptobenzthiazole: Flotagen and Flotagen S: influence of alkalies, cyanide and copper sulphate on adsorption by galena, sphalerite, pyrite and chalcopyrite, 53
Fluorite: flotation: froth: amenability, 89
Fluorspar: flotation: froth: bibliography, 100
      laboratory experiments, 89
      separation from gangue containing calcite, 89
      separation from quartz, 90
  market specifications, 89
  production: United States, 89
  waste from mill: mineral and particle size, 89
Fraas, F. and Ralston, O. C.: *Discussion on Selective Electrostatic Separation*, 419
Furnaces: Cooley roasting furnace, 392

G

Gahl, R.: *Discussion on Electrocapillary Amalgamation*, 273
Galena (*see also* Sulphide Minerals):
  flotation: mechanism, 31
    temperature influence, 41
Gardner, G. R. and Ray, K. B.: *Flocculation and Clarification of Slimes with Organic Flocculants*, 146
Gaudin, A. M.: *Discussion on Oil-air Separation of Nonsulphide and Nonmetal Minerals*, 202, 203, 204
Gilsonite: flotation: oil-air separation, 190
Gold: physical characteristics of gold lost in tailings: microscopic study, 256
  recovery from ore by simultaneous dissolution by cyanide and adsorption on activated charcoal, followed by recovery of charcoal by flotation, 207
Gold milling (*see also* Amalgamation, Cyanidation):
  chloridizing: Achotla mill, Mexico, 243
  coated particles: cleaning processes, 243, 254
  coated particles: responsible for losses, 256
  flotation of fines, Benguet, 224
  gold lost in tailings: suggestions for recovery, 262
  oxide ores: cyanidation: Demonstration Gold Mines, P.I., 236
  oxidized ore: washing and crushing: Hadsel mill, 239
  physical characteristics of gold lost in tailings: microscopic study, 256
    spectrographic study, 261
  refractory ores: treatment processes, 262
  sulphide ores: flotation: Demonstration Gold Mines, P.I., 236
  tarnished particles: responsible for losses, 256
Gold ore: grindability tests, 311
Gold-silver ore: Benguet: tellurides present, 227, 235
  chloridizing before cyanidation, 243
Graphite: flotation: oil-air separation, 187, 199, 201
Griffin, M. L.: *Discussion on A Study of the Flotative Properties of Hematite*, 126, 127
Grinding (*see also* Crushing and Grinding and Grindability):
  and classification: heavy-duty classifiers in closed-circuit grinding reduce costs and increase tonnage, 274
  ball-mill efficiency versus drop-weight device, 291
  ball sizes: effect, 290, 295, 322
  cement. *See* Cement.

Grinding: closed-circuit: circulating load: effect, 320
    circulating-load ratio vs. total tons mill pulp flow per unit mill volume, 274
    costs reduced by heavy-duty classifiers, 274
    selective overgrinding: screens versus classifier, 367
    tonnage increased by heavy-duty classifiers, 274
    with stainless-steel screens: blinding by corrosion or wood pulp absent, 361
      life of screens compared with that of ordinary steel screens, 364, 369
      little preferential grinding of sulphide materials, 361
    screens versus classifiers in circuit, 361
  coercive force: relation to work input, 286
    relation to work input for crushing magnetite, 324
    variation with specific surface and particle size, 284
  critical circulating load, 319
  efficiency: criterion, 315
    meaning of term, 316
    magnetite standard material for measuring, 324
    measurement by coercive force of magnetite, 282, 324
  Electric Ear: automatic control of operation of mills by their sound, 371
  fine: and classification: Hollinger Consolidated Gold Mines Ltd., 331
    change from two-stage to single-stage arrangement, 331
  formula for new surface area produced, 323
  magnetite: specific surface proportional to coercive force, 284
    work input proportional to increase in coercive force, 286
  mill capacity: screens versus classifiers, 369
  power input effect, 320
  principles: study with coercimeter on magnetite, 282
  rusting: effect on efficiency, 365
  65-mesh in closed circuit with stainless-steel screens, 361
  sound control: field of usefulness, 378
  sound: relation to useful grinding energy, 371
  total amount of work done important, 323
  useful and ultimate: comparison with various circulating loads, 288
  wet: blinding of screens prevented by submerging screen, 322
Grindability: cement clinker, 313
  copper ore, 297, 311
  effect of circulating load, 315
  gold ore, 297, 311
  petroleum coke, 313, 319
  various ores, record of tests, 296
Gross, H. E., Mitchell, D. R. and Oehler, H. E.: *Froth Flotation of Fluorspar*, 89

H

Hadsel mill: washing and crushing combined: oxidized gold ores, 239
Hahn, A. W.: *Discussion on Physical Characteristics of Gold Lost in Tailings*, 263
Hardinge Company, Inc.: the Electric Ear, for automatic control of operation of grinding mills by their sound, 371
Hardinge, H.: *The "Electric Ear,"* 371; *discussion*, 388
Hassialis, M.: *Discussion on Oil-air Separation of Nonsulphide and Nonmetal Minerals*, 203, 204
Hassialis, M., Taggart, A. F., Sadler, A. M. and del Giudice, G. R. M.: *Oil-air Separation of Nonsulphide and Nonmetal Minerals*, 180
Head, R. E.: *Mineralogical Characteristics Affecting the Concentration of a Semioxidized Lead-silver Ore*, 169; *discussion*, 179
  *Physical Characteristics of Gold Lost in Tailings*, 256; *discussion*, 264
Hematite: flotative properties: laboratory experiments, 102
  massive: definition, 127
    pure: preparation, 102
  specular; pure: preparation, 102
Hersam, E. A.: *Discussion on Electrocapillary Amalgamation*, 272
Hersberger, A. B. and Dean, R. S.: *New Flotation Reagents*, 81
Hitzrot, H. W.: *Improvements in Fine Grinding and Classification at the Hollinger Consolidated Gold Mines Ltd.*, 331
Hollinger Consolidated Gold Mines Ltd.: improvements in fine grinding and classification, 331
Holt-Dern process of chloridization, 244

I

International Nickel Co.: operation and tests of Electric Ear, 383
Iron ore: hematite. *See* Hematite.
Irvin, D. F.: *Discussion on Flocculation and Clarification of Slimes with Organic Flocculants*, 168

J

Jarman, G. W. Jr.: *Discussion on Selective Electrostatic Separation*, 421
Jarosites: analyses, 176
Jasberg, P. and Keck, W. E.: *A Study of the Flotative Properties of Magnetite*, 129
Johnson, H. B.: *Selective Electrostatic Separation*, 409; *discussion*, 422
Johnson, N. O.: *Comparative Washing Efficiencies in Cyaniding—The Washing Tray Thickener versus the Conventional Countercurrent Decantation Plant*, 424
Johnson, O. H.: *Discussions: on Closed-circuit Grinding of Cement Raw Materials at Leeds*, 359
  *Improvements in Fine Grinding and Classification at the Hollinger Consolidated Gold Mines Ltd.*, 343
Jordan, F. A.: *Discussions: on First Magnetic Roasting Plant in Lake Superior Region*, 406

JORDAN, F. A.: *Discussions: on A Study of the Flotative Properties of Hematite*, 127

K

KECK, W. E.: *Discussion on A Study of the Flotative Properties of Hematite*, 125 et seq.
KECK, W. E. AND JASBERG, P.: *A Study of the Flotative Properties of Magnetite*, 129
KECK, W. E., EGGLESTON, G. C. AND LOWRY, W. W.: *A Study of the Flotative Properties of Hematite*, 102
Kennecott Copper Corporation: rod-mill practice at Ray Mines, 327

L

Lake Superior region: magnetic roasting: first plant, 389
Lead minerals: oxidized: flotation: effect of sodium sulphide, alkalies and copper sulphate on effect of xanthate at mineral surfaces, 10,18
Lead-silver ore (*see also* Tintic District):
  floatability affected by mineralogical characteristics, 169
  semioxidized: mineralogical characteristics: microscopic study, 169
    that affect concentration, 169
LEE, O.: *Discussions: on First Magnetic Roasting Plant in Lake Superior Region*, 406
  *on A Study of the Flotative Properties of Hematite*, 127
LOCKE, C. E.: *Discussions: on A Cyanide Process Based on the Simultaneous Dissolution and Adsorption of Gold*, 221
  *on First Magnetic Roasting Plant in Lake Superior Region*, 406
  *on Mineralogical Characteristics Affecting the Concentration of a Semioxidized Lead-silver Ore*, 178
  *on Selective Electrostatic Separation*, 421, 422
  *on 65-mesh Grinding in Closed Circuit with Stainless-steel Screens*, 368
  *on A Study of the Flotative Properties of Hematite*, 128
LOWRY, W. W., KECK, W. E. AND EGGLESTON, G. C.: *A Study of the Flotative Properties of Hematite*, 102

M

Magnetic roasting: iron ore: Anzan, Manchuria, 406
  costs still too high for general use, 405
  first plant in Lake Superior region, 389
  Gijon, Spain, abandoned, 408
  moisture in ore: effect on plant operation, 401
  process, 389
Magnetite: flotative properties: laboratory experiments, 129
  grindability: coercimeter study, 282
  pure: preparation, 129
  standard material for measuring grinding efficiency, 324
MAXSON, W. L.: *Discussion on Grindability and Grinding Characteristics of Ores*, 317 et seq.
MAXSON, W. L. AND BOND, F. C.: *Grindability and Grinding Characteristics of Ores*, 296; *discussion*, 323
MCARTHUR, C. K.: *Modern Trends in Classification*, 274
MCLACHLAN, C. G.: *Discussion on Rod-mill Practice at Ray Mines Division, Kennecott Copper Corporation*, 329
Mercaptobenzthiazole. *See* Flotagen.
Metallic soaps: flotation, 192
Mexico: Achotla chloridizing mill, 243
Michigan College of Mining and Technology: study of: flotative properties of hematite, 102
    flotative properties of magnetite, 129
Microscopic study: mineralogical characteristics of semioxidized lead-silver ore that affect concentration, 169
MILLIKEN, F. R.: *Discussion on Closed-circuit Grinding of Cement Raw Materials at Leeds*, 359
MITCHELL, D. R., GROSS, H. E. AND OEHLER, H. E.: *Froth Flotation of Fluorspar*, 89
MORRIS, J. M.: *Milling Developments at the Benguet Consolidated Plant*, 224; *discussion*, 235
Murex process, flotation, 87

N

NEILL, J. W.: *Discussion on First Magnetic Roasting Plant in Lake Superior Region*, 406
New Cornelia Branch: Phelps Dodge Corporation: milling methods, 434
NORMAN, J. E. AND RALSTON, O. C.: *Conditioning Surfaces for Froth Flotation*, 65

O

OEHLER, H. E., MITCHELL, D. R. AND GROSS, H. E.: *Froth Flotation of Fluorspar*, 89
OLDRIGHT, G. L.: *Discussion on The Achotla Chloridizing Mill*, 255

P

Paraffin wax: flotation: oil-air separation, 190
Pendulum impact tests: measurement of surface energy of ore, 307, 317
PETERSON, E. C.: *Discussion on Mineralogical Characteristics Affecting the Concentration of a Semioxidized Lead-silver Ore*, 178
Petroleum coke: grindability tests, 313, 319
Phelps Dodge Corporation: New Cornelia: milling methods, 434
Philippine Islands: Benguet: milling developments: gold, 224
  Demonstration Gold Mines: milling practice, 236
Phosphate: flotation: calcium lauryl phosphate as activator, 205, 206
    oil-air separation: effect of slime in pulp, 196

Pittsburgh Coal Co.: experiments in flocculation and clarification of slimes with organic flocculants, 146

Pyrite (*see also* Sulphide Minerals):
  flotation: temperature influence, 41

Q

Quartz: flotation: oil-air separation: effect of iron, 194

R

Ralston, O. C.: *Discussion on Oil-air Separation of Nonsulphide and Nonmetal Minerals*, 198

Ralston, O. C. and Fraas, F.: *Discussion on Selective Electrostatic Separation*, 419

Ralston, O. C. and Norman, J. E.: *Conditioning Surfaces for Froth Flotation*, 65

Ray, K. B. and Gardner, G. R.: *Flocculation and Clarification of Slimes with Organic Flocculants*, 146

Rey, M.: *Discussion on Principles of Flotation*, 24

Roasting: iron ore. *See* Magnetic Roasting.

Roberts, E. J.: *Discussion on 65-mesh Grinding in Closed Circuit with Stainless-steel Screens*, 368

Rod mills: conversion to open-end ball mills, 335, 343
  Ray Mines Division, Kennecott Copper Corporation, 327

Roller, P. S.: *Discussion on Oil-air Separation of Nonsulphide and Nonmetal Minerals*, 204, 205

Rose, E. H.: *Discussion on 65-mesh Grinding in Closed Circuit with Stainless-steel Screens*, 366 et seq.

S

Sadler, A. M., Taggart, A. F., del Giudice, G. R. M. and Hassialis, M.: *Oil-air Separation of Nonsulphide and Nonmetal Minerals*, 180

Schuhmann, R. Jr.: *Discussion on Oil-air Separation of Nonsulphide and Nonmetal Minerals*, 197

Screens. *See* Grinding.

Shepard, N. L.: *Discussions: on Grindability and Grinding Characteristics of Ores*, 322
  *on 65-mesh Grinding in Closed Circuit with Stainless-steel Screens*, 370

Shepard, O. C.: *Electrocapillary Amalgamation*, 265
  *Discussions: on Grindability and Grinding Characteristics of Ores*, 317
    *on A Study of the Flotative Properties of Hematite*, 127

Silver-lead ores. *See also* Lead-silver ores.

Silver milling: chloridizing: Achotla mill, Mexico, 243
  coated particles: cleaning processes, 243, 254

Slimes: flocculation and clarification with starch solutions, 146

Snouffer, R. D.: *Discussion on Flocculation and Clarification of Slimes with Organic Flocculants*, 165

Sphalerite (*see also* Sulphide Minerals):
  flotation: temperature influence, 41

Stanford University: study of electrocapillary amalgamation, 265

Starch solutions for flocculation and clarification of slimes, 146

Stephen, W. M.: *65-mesh Grinding in Closed Circuit with Stainless-steel Screens*, 361

Sulphide minerals: flotation: influence of sodium sulphide, alkalies and copper sulphate on effect of xanthate at mineral surfaces, 13, 19

Sulphur: flotation: oil-air separation, 182, 198, 200

Sutherland, K. L. and Wark, I. W.: *Principles of Flotation, VII—Mercaptobenzthiazole as a Flotation Agent*, 53

Sweeney, E. L.: *Discussions: on a Cyanide Process Based on the Simultaneous Dissolution and Adsorption of Gold*, 222
  *on 65-mesh Grinding in Closed Circuit with Stainless-steel Screens*, 366

T

Taggart, A. F.: *Discussions: on Grindability and Grinding Characteristics of Ores*, 319
  *on Oil-air Separation of Nonsulphide and Nonmetal Minerals*, 205
  *on Principles of Flotation*, 39, 40
  *on A Study of the Flotative Properties of Hematite*, 126

Taggart, A. F., del Giudice, G. R. M., Sadler, A. M. and Hassialis, M.: *Oil-air Separation of Nonsulphide and Nonmetal Minerals*, 180

Tintic district: lead-silver ores: high recovery of both anglesite and cerussite necessary to increase recovery of metal, 177
  jarosites, 176
  loss in tailings, 177
  metallic silver, 172, 178
  semioxidized: mineralogical characteristics that affect concentration: microscopic study, 169

Tuck, F. J.: *Rod-mill Practice at Ray Mines Division, Kennecott Copper Corporation*, 327

U

U. S. Bureau of Mines: study of: coercimeter in grinding tests, 282
  conditioning surfaces for froth flotation, 65
  magnetite as standard material for measuring grinding efficiency, 324
  mineralogical characteristics affecting concentration of semioxidized lead-silver ore, 169
  new flotation reagents, 81
  physical characteristics of gold lost in tailings, 256

Universal Atlas Cement Co.: closed-circuit grinding of cement raw materials at Leeds, 344

University of Arizona: Chapman process of simultaneous dissolution and adsorption of gold, 207
University of Illinois: study of flotation of fluorspar, 89
University of Melbourne: study of principles of flotation, 7, 26, 41, 53
Utah: Tintic district. *See* Tintic.

W

WARK, I. W. AND COX, A. B.: *Principles of Flotation, IV—An Experimental Study of Influence of Sodium Sulfide, Alkalies and Copper Sulfate, on Effect of Xanthates at Mineral Surfaces*, 7
WARK, I. W. AND COX, A. B.: *Principles of Flotation*, V—*Conception of Adsorption Applied to Flotation Reagents*, 26
*Principles of Flotation*, VI—*Influence of Temperature on Effect of Copper Sulphate, Alkalies and Sodium Cyanide on Adsorption of Xanthates at Mineral Surfaces*, 41; *discussion*, 52
*Discussion on Oil-air Separation of Nonsulphide and Nonmetal Minerals*, 199
WARK, I. W. AND SUTHERLAND, K. L.: *Principles of Flotation*, VII—*Mercaptobenzthiazole as a Flotation Agent*, 53

X

Xanthates. *See* Flotation.

3 8198 309 333 118
THE UNIVERSITY OF ILLINOIS AT CHICAGO

THIS BOOK IS FOR USE
ONLY IN THE LIBRARY
IT DOES NOT CIRCULATE